ELECTROLYTIC CONDUCTANCE IN DIPOLAR APROTIC AND MIXED SOLVENT SYSTEMS

BY

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This dissertation is dedicated to my parents, who made it all possible.

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KEY TO SYMBOLS

a	Distance of closest approach of ions
A	Coefficient of Kohlrausch conductance relation
A	Pitts conductance term
A	Debye-Hückel parameter
b	$z^2e^2/a\varepsilon kT$
B	Debye-Hückel parameter
B	Pitts conductance term
c	Concentration in mol L^{-1}(M)
C	Velocity of light
C	Capacitance
e	Protonic charge
E	Expanded conductance equation parameter
$f_\pm$	Mean ionic activity coefficient on mole fraction scale
F	Force acting on ion
G	Pitts conductance term
H	Pitts conductance term
I	Ionic strength
J_1	Expanded conductance equation parameter
J_2	Expanded conductance equation parameter
k	Boltzmann's constant
K_a	Association constant
K_d	Dissociation constant
M	Molecular weight
n	Number of points
N	Avogadro's number
q	Bjerrum's distance ($z^2e^2/2\varepsilon kT$)
R	Resistance (absolute Ω)
S	Coefficient of Debye-Hückel-Onsager limiting law
S_1	Pitts conductance term
t^o	Transport number
T	Absolute temperature
T_1	Pitts conductance term
v	Ionic velocity
X	Mole fraction
y	κa
$y_\pm$	Mean ionic activity coefficient on molar scale
z	Charge on ion

α	Degree of dissociation
α	Relaxation coefficient of D-H-O limiting law
β	Electrophoretic coefficient of D-H-O limiting law
ε	Dielectric constant
η	Viscosity (Poise)
θ	Cell constant
κ	Specific conductance
κ	$(8\pi Ne^2I/1000\varepsilon kT)^{\frac{1}{2}}$
λ	Ionic conductance
λ^o	Limiting ionic conductance
Λ	Equivalent (or molar) conductance
Λ^o	Limiting equivalent conductance
Λ_i	Ionic equivalent conductance
ν	Frequency
ρ	Density
σ	Standard deviation
ω	Radial frequency $(2\pi\nu)$

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There has been much interest in the study of the properties of electrolytes in dipolar aprotic solvents. Two such solvents were chosen for this study: sulfolane, and 1-methyl-2-pyrrolidinone (NM_2Py). The electrolyte chosen for this study was hydrogen chloride (HCl), a stong electrolyte in water. The conductimetric behavior of HCl was studied in sulfolane and sulfolane-water solvents at 25, 30, and 40°C, and in NM_2Py and NM_2Py-water solvents at 25°C. A study was made of the conductimetric behavior of sodium chloride (NaCl), sodium acetate (NaAc), tris(hydroxymethyl aminomethane hydrochloride (Tris·HCl), acetic acid (HAc), and HCl in the mixed solvent containing 80 weight-% 2-methoxyethanol and 20 weight-% water (80 W% MetOH-H_2O).

Conductances were measured with fill cells of the Kraus type, in conjunction with a transformer bridge based on the design of Janz and McIntyre. Measurements were made at 2.5, 5.0, and 10.0 kHz and extrapolated to obtain the true ohmic resistance by the method of Hoover. The conductance data were analyzed with the full Pitts equation, setting the ion size parameter equal to the Bjerrum critical distance. Analyses were also made with log-log plots and the Shedlovsky-Kay extrapolation. A comparison of the full and expanded conductance equations was also made.

The study of the sulfolane solvent systems showed increasing ion association and decreasing limiting equivalent conductance with increasing sulfolane content. In pure sulfolane, HCl was found to exist primarily in an associated form, with evidence of homoconjugation with chloride. There was evidence of a change in the dissociation process for HCl in pure sulfolane with increasing temperature.

The study of HCl in the NM_2Py solvent systems showed a sharp decrease in limiting equivalent conductance with increasing NM_2Py content, coupled with a gradual increase in ion association. As opposed to sulfolane, NM_2Py gave evidence of being able to solvate the proton. For both sulfolane and NM_2Py, the electrostatic models of ion association were generally unable to predict the amount of association that was found.

Both of the dipolar aprotic solvents studied gave evidence of disrupting the water structure, with sulfolane causing a decrease in the over-all structuring of the solvent. The NM_2Py was found to cause an increase in the structuring of the solvent, with evidence of the formation of an associated species of the form $NM_2Py \cdot 2H_2O$.

In the study of the 80 W% MetOH-H_2O, all electrolytes studied, except HAc, were found to be slightly associated. The conductance of Tris·HCl in water was studied, and a comparison between the two systems was made. Acetic acid was found to exist in a primarily associated form, with the dissociation constant comparable to that found in other such alcohol-water solvents.

CHAPTER I

INTRODUCTION

The last two decades have seen a growing interest in that class of solvents characterized as being both dipolar and aprotic. Some of these solvents, such as acetonitrile, have been extensively studied;[1-6] others have been less well characterized. One such is sulfolane (tetrahydrothiophene-1-1-dioxide, tetramethylene sulfone). One reason for this lack of research may be that sulfolane is a solid at room temperature, requiring measurements at temperatures of 30°C or above. Yet despite this drawback, sulfolane remains an excellent solvent.[7-8] Possessing a moderately high dielectric constant,[9] sulfolane would be expected to reduce the ion-ion interactions found in solvents with smaller dielectric constants. With its high dipole moment[10] it would be expected to increase ion-dipole interactions. For both these reasons, sulfolane is expected to have a moderate solvating power. Sulfolane has been characterized[11-12] as having extremely weak acid-base properties, facilitating the study of strong acids and bases.

Another of the lesser dipolar aprotic solvents is 1-methyl-2-pyrrolidinone. For the same reasons cited for sulfolane it is expected to have moderate solvating power;

it is, however, more basic than sulfolane,[8] and has been shown to enter into extensive hydrogen bonding with water,[13] something which is not true of sulfolane.[14] It would be of interest then to compare the behavior of electrolytes in these two dipolar aprotic solvents.

A far more common class of solvents is that considered to be protic, the most common of these being water. One of the lesser studied of this class of solvents is the mixed solvent consisting of 80 weight percent 2-methoxyethanol (methyl cellosolve) and 20 weight percent water. First studied by Simon[15] in the middle fifties, a number of studies have since been published regarding this solvent,[16-18] but questions about the behavior of electrolytes within it remain.[17]

Conductance studies have been shown[19] to be an excellent tool for characterizing the behavior of electrolyte solutions, due in part to the great accuracy attainable.[20] It is the major tool employed in these studies.

CHAPTER II

THEORY

General Background

The resistance of a uniform cross section of a homogeneous substance, with length l and area A is given by the equation:

$$R = \frac{l}{A\kappa} \tag{1}$$

where κ is a constant called the specific conductance and is characteristic of the material under study. If a conductivity cell had a uniform cross sectional area and electrode separation, then by measuring the resistance of a solution we could obtain the specific conductance. Since cell geometry varies with manufacture, however, it becomes necessary to introduce a parameter called the cell constant. This will have units of length divided by area and can be determined by measuring the resistance of a solution whose specific conductance is known. The relationship between specific conductance and cell constant is:

$$\kappa = \frac{\theta}{R} \tag{2}$$

Since the conduction of electricity by an electrolyte solution depends on ions as the charge carriers, the specific conductance will vary with the concentration of ions.

By dividing the specific conductance by the concentration we obtain a conductance per mole, useful for making comparisons between solutions of differing concentrations. This is the molar conductance, also known as the equivalent conductance. It is defined by the equation:

$$\Lambda = \frac{1000\kappa}{c} = \frac{1000\theta}{Rc} \tag{3}$$

where c is the molar concentration. The resistance is usually corrected for the conductance due to the solvent:

$$\frac{1}{R} = \frac{1}{R_m} - \frac{1}{R_{solv}} \tag{4}$$

where R_m is the measured resistance and R_{solv} is the solvent resistance. In this study the terms equivalent conductance and molar conductance are used interchangeably, since for a 1:1 electrolyte, such as is studied here, equivalents per liter and moles per liter are identical.

It was in 1883 that Arrhenius, by studying the varying conducting power of solutions came to the conclusion that electrolytes could supply varying amounts of ions depending on the electrolyte concentration. He concluded that as the concentration tended toward zero (infinite dilution), the degree of dissociation, α, tended toward unity. Noting that at a fixed temperature Λ increased as concentration decreased, he ascribed this to increasing dissociation. Thus at infinite dilution, Λ would reach a maximum value, Λ^o, which would correspond to the conductance for a totally dissociated electrolyte, and the degree of dissociation at any given concentration could be expressed as a ratio of the molar conductance at the concentration to the molar conductance at infinite dilution:

$$\alpha = \frac{\Lambda}{\Lambda^o} \tag{5}$$

From this, Ostwald later derived the famous dilution law:

$$K_d = \frac{\alpha^2 c}{(1 - \alpha)} = \frac{\Lambda^2 c}{\Lambda^o(\Lambda^o - \Lambda)} \tag{6}$$

This was in accord with the Arrhenius proposition that at low concentrations the molar conductance should vary in a linear manner with the concentration.[21]

However, Kohlrausch, a contemporary of Arrhenius, had made some precise measurements of the conductance of solutions at low concentrations, and he came to the conclusion that Λ varied with $c^{\frac{1}{2}}$ and followed the relation:[22]

$$\Lambda = \Lambda^o - Ac^{\frac{1}{2}} \tag{7}$$

There were sets of data which conformed to one theory; there were data sets which conformed to the other. This seeming paradox held sway for many years.

Measurement of Conductance

Before proceeding further, a few words are in order on how the conductance of a solution is measured. Such measurements are extremely sensitive and require very careful technique in order to insure accurate results. As Shedlovsky has pointed out,[23] the resistance measured for a solution will change approximately 2% per °C; to have a precision of 0.01% thus requires that the temperature be regulated to 0.005°C or better. This is but one of several factors that need to be considered in conductance measurements.

When determining conductance one is actually measuring the resistance of a solution. As with most precision resistance measurements, some variant of Wheatstone's bridge is usually used. A schematic diagram of such a bridge appears in Figure 1. The circuit is such that, when the detector registers a null (i.e., there is no current flowing in the circuit) the following balance condition is met:

$$\frac{R_c}{R_1} = \frac{R_s}{R_2} \quad . \tag{8}$$

R_1 and R_2 are precision resistors whose values are known (and preferably equal); thus at null, the cell resistance is equal to the resistance set on the standard.

Such a bridge was designed primarily for direct current measurements. However, if a direct current is applied to an electrolyte solution there will be migration of ions to the electrodes; this electrolysis will produce a change in

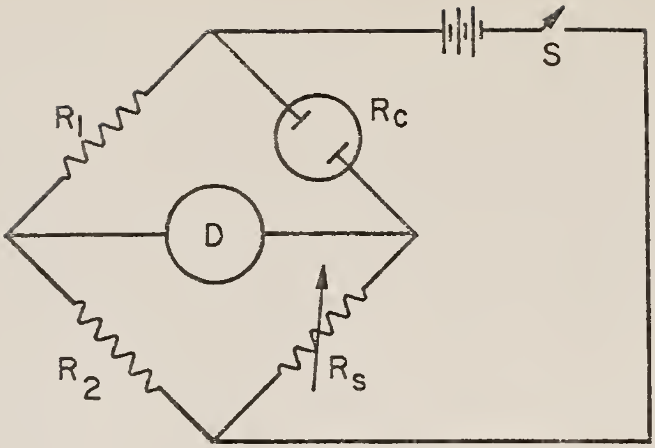


Figure 1

Wheatstone's Bridge

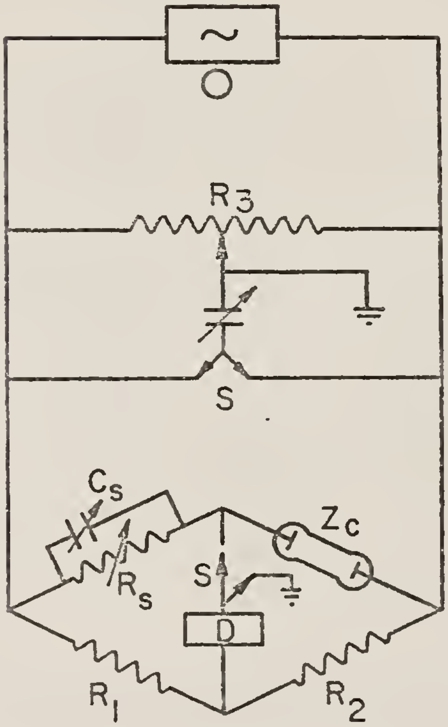


Figure 2

Jones -- Joseph Conductivity Bridge

the solution concentration and a concomitant change in the resistance.

Initially, it was Kohlrausch who proposed to solve this problem by the use of alternating current for resistance measurements. This, however, introduces a problem of its own. Given the parallel plate configuration of most conductance cells, there will arise a capacitance due to the flow of alternating current through the cell. This means that the bridge must not only balance resistances, it must now balance capacitances as well. As a result, modern bridges are designed to balance impedance.

A great deal of the early work on bridge design and conductance measurement was done by Shedlovsky,[20] Parker,[24] Jones and his students[25,26,27,28,29] and others. Much of this early work has been summarized elsewhere[30] and will not be covered in any great depth here. A typical bridge circuit designed to measure the impedance of a conductance cell[25] is presented in Figure 2. In more recent times, Ives and his coworkers have demonstrated[31] the usefulness of the transformer bridge circuits found in commercial impedance comparators. This study utilized just such a bridge, designed by Janz and McIntyre.[32] It will be described in more detail in a later chapter.

When measuring resistance with such a bridge, a dependence of resistance on the frequency of the alternating current used is unavoidable. For precise measurements to have any meaning, there must be some way to eliminate this frequency dependence and obtain the true ohmic resistance. A large amount of the frequency dependence has been found to be caused by extraneous factors and can be removed by proper cell design[24,33] and the use of a proper thermostating medium.[25]

Platinization of the electrodes helps to reduce the remaining frequency dependence greatly,[34] and is of great aid when measuring the conductance of concentrated solutions; in dilute solutions, the large surface area of the platinum black favors adsorption of the electrolyte under study.[23] Consequently, in this study, shiny platinum electrodes were used.

A conductance cell may be schematically represented as shown in Figure 3:

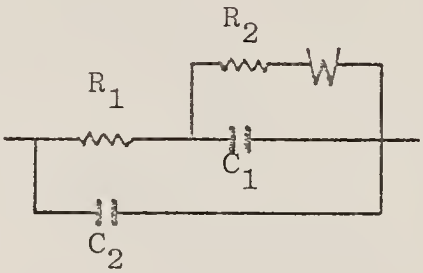


Figure 3
Circuit equivalent to conductance cell.

This circuit was proposed by Ives and his coworkers[31] and endorsed by Robinson and Stokes, who added the Warburg impedance, -W-.[34] In this circuit, R_1 is the true ohmic resistance of the cell, which is what we wish to determine. This is independent of frequency over the limited range of measurement (between 1 and 10 kHz). In series with R_1

is the capacitance C_1, due to the double layer. This is also expected to be independent of frequency in the range of frequencies used in this study. It is this capacitance which in fact is responsible for transporting through the double layer the current passing through R_1; it has been shown that a cell has a definite resistance with only a few millivolts of potential applied, too small a potential to cause electrolysis at the electrodes. There is, however, a small amount of electrolysis which takes place, probably due to discharge of solvent ions, and this is represented by "faradaic leakage" in parallel to the double layer. It is represented by resistance R_2 and the Warburg impedance, both of which are expected to vary with $\omega^{-\frac{1}{2}}$. Capacitance C_2 is the capacitance due to the leads and connections, and in cells such as were used in this study it is negligible.[34]

Ives[31] has assumed a negligible Warburg impedance and determined the frequency dependence of the measured resistance to be of the form:

$$R_m = R_1 + \frac{R_2}{1 + a\omega^2} \qquad (9)$$

where:

$$a = \frac{R_1 R_2{}^2 C_1{}^2}{R_1 + R_2}$$

and:

$\omega = 2\pi\nu$, ν being the frequency.

Hoover[35] has compared a number of models for bridge balance conditions and has come to the conclusion the model proposed by Ives is of sufficient accuracy to use for the extrapolation to remove the frequency dependence and obtain the true ohmic resistance. A more detailed discussion of this frequency extrapolation method appears in a later chapter.

Over the years there have been a large number of cell designs for the measurement of electrolytic conductance. For the purposes of this study a cell of the Kraus design[36] was used. This type of cell helps to eliminate several sources of error, including some sources of frequency dependence in the measured resistance alluded to above. A discussion of this style of cell appears in the experimental section along with a photograph of the cell actually used.

Conductivity Equations

As mentioned previously, in the early days of conductance studies there was something of a paradox. The Ostwald dilution law, based on the Arrhenius theory of dissociation, indicated a linear dependence of equivalent conductance on concentration and there were data to back it up. Yet Kohlrausch showed a dependence, not on c but on $c^{\frac{1}{2}}$, and had data to confirm the variation. Kohlrausch had also proposed his law of independent migration, which, succinctly stated, says that the limiting conductance (the conductance at infinite dilution) is equal to the sums of the limiting conductances for the individual ions:

$$\Lambda^{o} = \lambda_{+}^{o} + \lambda_{-}^{o} \tag{10}$$

there being no interaction between moving ions at infinite dilution. Since it is unlikely that both ions will contribute identically to the total conductance, the fraction carried by one ion may be expressed by the transport number t^{o}:

$$t_{+}^{o} = \frac{\lambda_{+}^{o}}{\Lambda^{o}} \tag{11}$$

The expression for the negative ion is identical, and thus from Equation 10 one finds:

$$t_{+}^{o} + t_{-}^{o} = 1 \tag{12}$$

The paradoxical problem continued to plague conductivity through the first several decades of this century. In 1923, Debye and Hückel[37] proposed their theoretical treatment of interionic interactions, and this was further applied to conductance studies in 1927 by Onsager.[38] This combined Debye-Hückel-Onsager theory was the first major attempt to theoretically account for the variation of conductance with concentration.

In an electrolyte solution placed under the influence of an external electric field there are two major interionic interactions: the electrophoretic effect and the relaxation effect. These have been extensively discussed elsewhere[34,39] and thus will be dealt with in a more succinct manner here.

The electrophoretic effect arises from viscous drag. An ion moving through a solution will tend to drag along solvent molecules with it, both through frictional forces and through having solvent molecules associated with the ion (solvating the ion). Neighboring ions will thus experience a net solvent flow, in the direction of their movement if they are the same charge type as the central ion, and against their motion if of opposite sign to the central ion. Quite clearly, this effect will decrease as the concentration of ions decreases, and will reach zero at infinite dilution.

It has been shown[34] that the electrophoretic increment to the velocity of the ion is given by the equation:

$$v_- = \sum_{n=1}^{\infty} A_n \cdot \frac{z_-^n(z_-^{n-1}k_- - z_+^{n-1}k_+)}{a^n(z_- - z_+)} \qquad (13)$$

where n arises from Boltzmann distribution functions, k is the force acting on the ion, and A_n is given by:

$$A_n = \frac{(-1)^n}{n!6\pi\eta}\left(\frac{e^2}{\varepsilon kT}\right)^{n-1}\Phi_n(\kappa a) \tag{14}$$

The function $\Phi_n(\kappa a)$ is given by:

$$\begin{aligned} \Phi_n(\kappa a) &= (\kappa a)^2\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^n S_n(\kappa a) \\ S_n(\kappa a) &= a^{n-2}\int_a^\infty \frac{e^{-n\kappa r}}{r^{n-1}}\,dr \end{aligned} \tag{15}$$

κ in this case is not the specific conductance, but the Debye-Hückel reciprocal radius of the ionic atmosphere, and a is the distance of closest approach of the ions; κ is given by:

$$\kappa = \left(\frac{8\pi Ne^2 I}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{16}$$

with the remainder of the symbols having their usual meanings.

The relaxation effect arises as follows. The ion being studied is at the center of an atmosphere of spherical distribution. If the central ion moves, the atmosphere will move with it, but a little more slowly, As a result, the ion feels a net restoring force in the direction opposite to its motion, until the atmosphere has once again assumed the spherical symmetry. If the field acting on the ion is designated by X, then the relaxation field may be denoted as ΔX. Initially, Debye and Hückel examined the relaxation field, but it was elaborated by Onsager. For the 1:1 electrolytes we are concerned with in this study, the expression derived by Onsager is:

$$\frac{\Delta X}{X} = \frac{z^2e^2}{3\varepsilon kT} \cdot \frac{q\kappa}{1 + \sqrt{q}} \qquad (17)$$

where q is a function of charge z and ionic conductance at infinite dilution λ^o. For a 1:1 electrolyte its value is ½. The velocity of the ion, corrected for the relaxation effect becomes:

$$v_j = v_j^o \left(1 + \frac{z_1z_2e^2}{3\varepsilon kT} \cdot \frac{q\kappa}{1 + \sqrt{q}}\right) \qquad (18)$$

The effective force acting on a moving ion must be equal and opposite to the force of the external field[40] and may be expressed as:

$$-z_jeX = F_j^{vis} + F_j' + F_j'' \qquad (19)$$

where F_j^{vis} is the viscous drag of the solvent on the moving ion, F_j' is due to the electrophoretic effect, and F_j'' is due to the relaxation effect. It might be noted that at infinite dilution F_j'' and F_j' decrease to zero, and it is thus F_j^{vis} which determines the limiting conductance, λ_j^o.

Combining all of the above factors, Onsager derived what has come to be known as the Debye-Hückel-Onsager limiting law:

$$\Lambda = \Lambda^o - \frac{z^2e^2}{3\varepsilon kT} \cdot \frac{\Lambda^o q\kappa}{1 + \sqrt{q}} - \frac{F^2}{6\pi\eta N}(2z)\kappa \qquad (20)$$

For a 1:1 electrolyte, this reduces to:

$$\Lambda = \Lambda^o - Sc^{\frac{1}{2}} \qquad (21)$$

where:

$$S = \alpha\Lambda^{o} + \beta$$

$$\alpha = 82.0460 \times 10^{4} \frac{z^{3}}{(\varepsilon T)^{1.5}} \tag{22}$$

and:

$$\beta = 82.487 \frac{z^{3}}{\eta(\varepsilon T)^{\frac{1}{2}}}$$

As can be seen, the final equation has the same form that was empirically determined by Kohlrausch, the same dependence on $c^{\frac{1}{2}}$. But now, the constant S has a theoretical basis.

Since the equation was first proposed by Onsager, there have been numerous treatments devised. Most of them concentrate on elaborating the terms for the relaxation field, while the electrophoretic effect has also been modified. Shedlovsky[20] proposed a form of the limiting law suitable for extrapolation to determine Λ^{o}. Robinson and Stokes[41] did much the same but included a parameter to reflect finite ion size. Shedlovsky and Kay devised[42] an extrapolation for very weak (i.e., highly associated) electrolytes, based on an earlier treatment by Fuoss and Shedlovsky.[43]

Today, there are two main equation systems for analyzing conductance data. One is the result of many successive treatments by Fuoss and his coworkers.[44,45-47] The other is based on a theoretical treatment by Pitts.[48-50]

Both theories are quite complex, with the main equations containing several exponential integrals. Both have been expanded[51,52] to the same form:

$$\Lambda = \Lambda^{o} - Sc^{\frac{1}{2}} + Ec\log c + J_1 c - J_2 c^{1.5} \qquad (23)$$

In both terms, the constants S (the Onsager limiting law slope) and E are identical. The terms J_1 and J_2 differ depending on the theory used; it is these terms which contain the so-called ion-size parameter. This will be discussed in depth in the discussion chapter.

The equations, in the expanded format, are as follows:[40]

$$b\mathit{a} = \frac{z^2 e^2}{\varepsilon kT} = 16.7099 \times 10^4 \, \frac{z^2}{\varepsilon T}$$

$$\kappa = 50.2916 \, \frac{z\sqrt{c}}{(\varepsilon T)^{\frac{1}{2}}}$$

$$E = E_1 \Lambda^{o} - E_2$$

$$E_1 = \frac{(\kappa ab)^2}{24c} = 2.94257 \times 10^{12} \, \frac{z^6}{(\varepsilon T)^3}$$

$$E_2 = \frac{\kappa ab\beta}{16c^{\frac{1}{2}}} = 4.33244 \times 10^7 \, \frac{z^5}{\eta(\varepsilon T)^2}$$

$$J_1 = 2E_1\Lambda^{o}\left(\ln\left(\frac{\kappa\mathit{a}}{c^{\frac{1}{2}}}\right) + \Delta_1\right) + 2E_2\left(\Delta_2 - \ln\left(\frac{\mathit{a}}{c^{\frac{1}{2}}}\right)\right)$$

$$J_2 = \frac{\kappa\mathit{a}b}{c^{\frac{1}{2}}}\left(4E_1\Lambda^{o}\Delta_3 + 2E_2\Delta_4\right) - \Delta_5$$

The delta functions are complex, and may be obtained in Reference 40. Their values depend on the theory being used. They are for the Pitts equation and the latest of the Fuoss equations, that of Fuoss and Hsia,[44] both of which have been expanded by Fernández-Prini and Prue.[52]

In recent years, there has been a great deal of discussion as to which of the theories and its associated equations best fits the experimental data available. What is truly remarkable is that this has been going on for better than a decade and a half and there is still no conclusive proof that one theory is better than the other. That being the case, the theory used for data analysis is really serendipitous, depending on individual whim.

As will be mentioned in a following chapter, the expanded equations given above are approximations only and tend to break down at high concentrations (i.e., where κa becomes relatively large). For this reason, the data of this study were analyzed with the full Pitts equation described below.

The Pitts conductivity equation takes the general form:

$$\Lambda = \Lambda^o - \Lambda^o \left(\frac{A\sqrt{c}}{(1 + y)(\sqrt{2} + y)} + BcS_1\right) + G\sqrt{c}\left(\frac{1}{(1 + y)} - \frac{A\sqrt{c}}{(1 + y)^2(\sqrt{2} + y)} - \frac{H\sqrt{c}}{(1 + y)} T_1\right) \tag{24}$$

where:

$$A = H(\sqrt{2} - 1)$$

$$B = 3H^2$$

$G = \dfrac{\varepsilon kTHN10^9}{\pi\eta C^2}$, C is the velocity of light

$$H = \frac{z^2 e^2 \kappa}{3\varepsilon kT\sqrt{c}}$$

$$S_1 = \frac{9\sqrt{2} - 10 + y(3\sqrt{2} + 1) + 2y^2}{8(1 + y)^2(\sqrt{2} + y)^2} - \frac{e^Y}{4(1 + y)} E_i(y)$$

$$+ \frac{7\sqrt{2}}{16} \left(\frac{e^{(2 + \beta)y}}{(1 + y)^2(\sqrt{2} + y)}\right) E_i \left((\beta + 2)y\right)$$

$$+ \frac{\sqrt{2}}{16} \left(\frac{e^{(1 + \beta)y}}{(1 + y)(\sqrt{2} + y)}\right) E_i \left((\beta + 1)y\right)$$

$$T_1 = \frac{3}{4(\sqrt{2} + y)} + \frac{3}{8} \left(\frac{3\sqrt{2}e^{(\beta + 1)y}}{\sqrt{2} + y} E_i \left((\beta + 1)y\right) - 2e^y E_i(y)\right)$$

$$E_i(x) = \int_x^\infty \frac{e^{-u}}{u} du$$

$$y = \kappa a, \text{ where } \kappa = \left(\frac{8\pi N z^2 e^2 c}{1000\varepsilon kT}\right)$$

$$\beta = \frac{1}{\sqrt{2}}$$

All other symbols have their usual meaning. Values for the physical constants are taken from Reference 53.

This equation applied to dissociated electrolytes. To make it applicable to associated electrolytes, concentrations (c) were replaced by ionic concentrations (αc), where α is the degree of dissociation. Similarly, the calculated equivalent conductance calculated by the program, Λ_i, which is the conductance for a completely dissociated electrolyte, was multiplied by the degree of dissociation to get the equivalent conductance, according to equation 25:

$$\alpha = \frac{\Lambda}{\Lambda_i} \qquad (25)$$

The association constant, K_a, can be derived from the mass-balance equation utilizing the degree of dissociation:

$$K_a = \frac{1 - \alpha}{\alpha^2 c y_\pm^2} \tag{26}$$

In equation 26, $y_\pm$ is the mean activity coefficient on the molar scale. For low ionic strength media such as were studied, the activity coefficient can be calculated with the Debye-Hückel law:

$$f_\pm^2 = 10^{-\frac{2Az^2\sqrt{I}}{1 + B\alpha\sqrt{I}}} \tag{27}$$

where A and B are the usual Debye-Hückel parameters:

$$A = \frac{1.8246 \times 10^6}{(\varepsilon T)^{1.5}}$$

$$B = \frac{50.29 \times 10^8}{(\varepsilon T)^{\frac{1}{2}}} \tag{28}$$

This yields the activity coefficient on the mole fraction scale. To obtain the coefficient on the molar scale requires a conversion factor:

$$y_\pm^2 = \left(\frac{\rho}{\rho + 10^{-3}c2M_{\text{solvent}} - M_{\text{solute}}}\right)^2 f_\pm^2 \tag{29}$$

where:

M = molecular weight

ρ = density of solvent

The computer program, called "PITTSEQN," designed to perform the calculations associated with the Pitts theory is described in more detail in a following chapter.

CHAPTER III

EXPERIMENTAL

Materials

Solvents

Sulfolane was obtained from Eastman, a division of the Eastman Kodak Company. The material obtained was of a practical grade and was purified by a double distillation at reduced pressure.[52,54] The first distillation was at 2 torr pressure, stripping the boiling material with nitrogen. The second distillation was at 0.5 torr, from solid potassium hydroxide. The middle 75% was collected in each case, and in the final distillation it came off at 104°C. The product had a specific conductance of 4.09×10^{-8} S cm^{-1}.

1-Methyl-2-pyrrolidinone was obtained from Eastman, and was reagent grade. It was purified by double distillation at reduced pressure, both distillations being conducted at 0.5 torr pressure. The second distillation was from solid sodium hydroxide. The middle 75% was collected in each case, and the final product had a specific conductance of 3.64×10^{-7} S cm^{-1}.

2-Methoxyethanol was obtained from Eastman, and was reagent grade. It was purified by a single distillation at atmospheric pressure. The middle 75% was collected. When the 80 weight-% solvent was prepared, it was found to have a specific conductance of 1.11 x 10^{-7} S cm^{-1}.

Conductivity water was prepared by the distillation of water which had previously been treated by reverse osmosis followed by passage through a deionizing system. The specific conductance of this water was found to be in the range on 7-9 x 10^{-7} S cm^{-1}, quite reasonable since no effort was made to protect it from CO_2 in the atmosphere.

Reagents

Potassium chloride (for determination of the cell constants) was Mallinckrodt Analytical Reagent Grade, purified by double recrystallization from conductivity water. Tris base (tris(hydroxymethyl)aminomethane) was obtained from Sigma Chemical Company and was their Trizma Reagent Grade. It was purified by double recrystallization from 70% methanol-water. Sodium acetate and sodium chloride were Mallinckrodt Analytical Reagent Grade materials; they were recrystallized from water. After recrystallization, all salts were dried *in vacuo* at 75°C overnight and were stored in a desiccator which was charged with indicating Drierite.

The glacial acetic acid used was Mallinckrodt Analytical Reagent Grade and was purified by several fractional freezings. The final fraction was stored in a desiccator charged with indicating Drierite.

Solutions of hydrogen chloride were prepared by the double distillation, at atmospheric pressure, of analytical reagent grade hydrochloric acid, to obtain the constant boiling acid-water azeotrope. The final concentration of this azeotrope was determined by gravimetric determination of chloride with silver nitrate; its composition was found to be 5.27335×10^{-3} mol HCl per gram of solution.

Hydrogen chloride gas was prepared in two manners. In the early portions of the study, it was prepared by dropping redistilled hydrochloric acid onto reagent grade phosphorus pentoxide. The resulting hydrogen chloride gas was forced, by a stream of dry nitrogen, through a tower of indicating silica gel, and into a flask containing the solvent. In the latter portions of the study, the gas was prepared by dropping reagent grade sulfuric acid onto analytical reagent grade sodium chloride. The resulting gas was passed into the solvent via the method described above.

The concentrations of the acid solutions thus prepared were determined as follows. A solution of analytical reagent grade sodium hydroxide in water was prepared and was titrated pH-metrically against NBS primary standard potassium acid phthalate. This sodium hydroxide solution was then used in the pH titration of the acid solution.

Approximately 0.5 g of acid solution was weighed into a beaker containing about 100 ml of conductivity water. After mixing, this was titrated with the sodium hydroxide solution, using a microburet. In the titrations, consistently sharp endpoints were noted.

The concentration of the solution of hydrogen chloride in sulfolane thus determined was 1.1155×10^{-4} mol HCl g soln^{-1}. For the solution of hydrogen chloride in 1-methyl-2-pyrrolidinone, it was found to be 5.8359×10^{-4} mol HCl g soln^{-1}. Upon adding hydrogen chloride gas to sulfolane a color change was noticed. This intensified with time, until a deep golden hue was attained. This observation raised questions about the purity of the sulfolane, and tests were carried out to determine its purity.

At first, infrared spectroscopy was used. Figure 4 is the resulting spectrogram. Superimposed on it is a reference spectrogram.[55] Both the sulfolane solvent and the sulfolane containing HCl gave identical spectrograms, with no evidence of a major impurity.

A second test was ^{13}C nuclear magnetic resonance spectroscopy. Figure 5 is the spectrogram obtained, with the reference spectrogram superimposed.[55] Again, there was no noticeable trace of other material.

Finally, liquid chromatography was utilized in an attempt to determine any trace impurities. Figure 6a shows the chromatogram of the purified sulfolane; Figure 6b shows the chromatogram of sulfolane containing hydrogen chloride. Neither shows any impurity in sufficient quantity to affect the results of this study. It was concluded that despite the formation of the color, the sulfolane utilized for this study was pure.

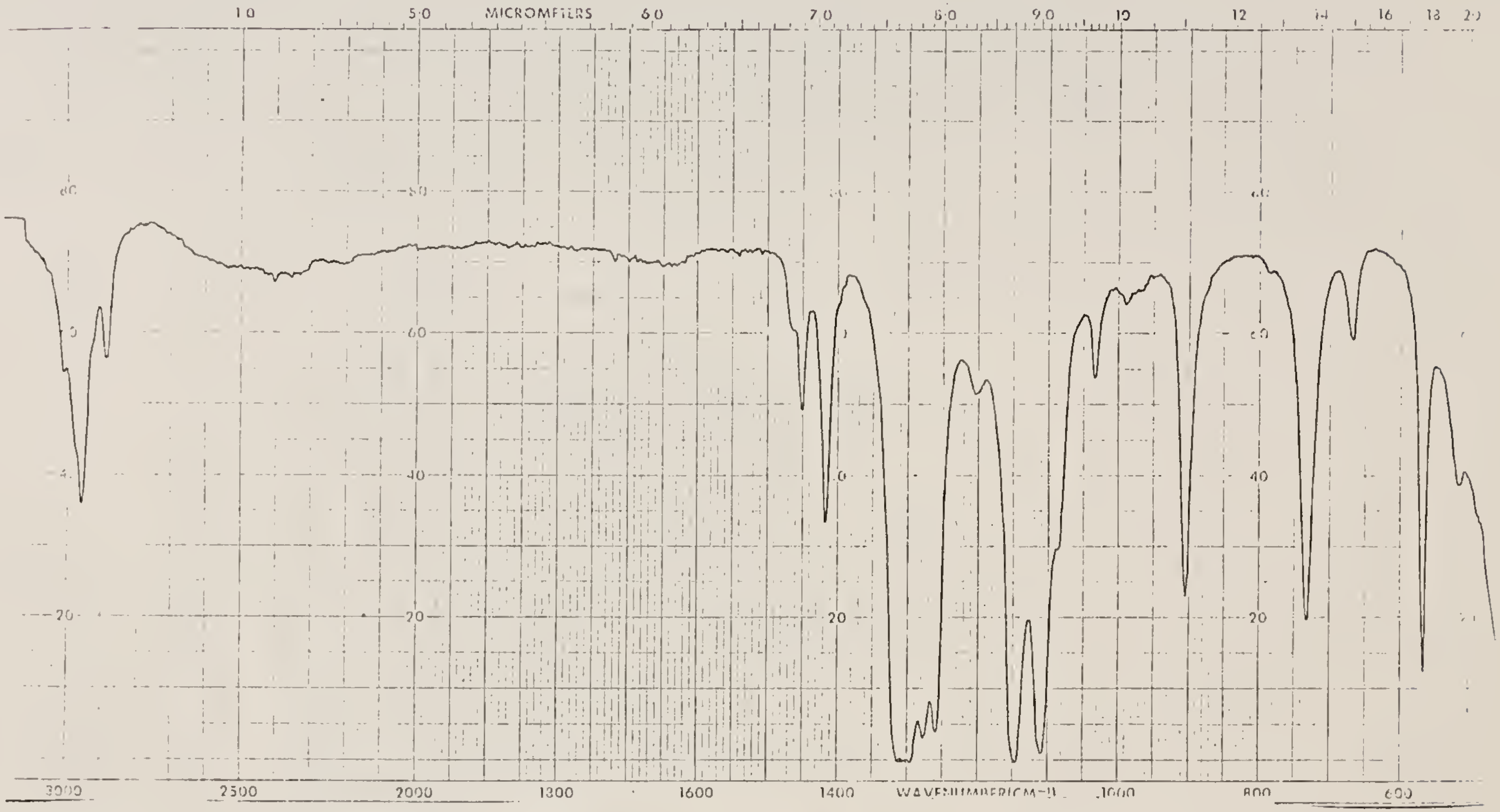
Acid solutions in mixed dipolar aprotic-water solvents were prepared by one of two methods. For those solvents with a large mole fraction of the nonaqueous component, the reagent was prepared by dilution of the stock solution of acid in the pure solvent. Water was added to bring the solution to the proper solvent composition, and the resulting solution was diluted to produce the working stock solution.

For those solvents relatively rich in water, the acid stock solution was prepared by adding the nonaqueous component to redistilled hydrochloric acid to achieve the proper solvent mix. This was then diluted to produce the working stock solution.

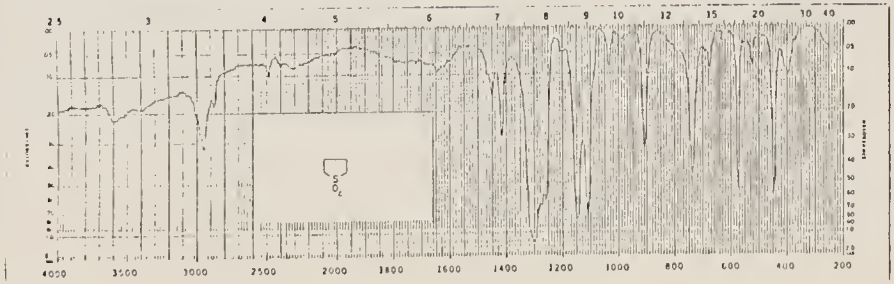
All stock solutions for the conductance measurements were prepared on a strictly weight basis.

Figure 4

Infrared spectrogram of sulfolane and sulfolane-HCl



TETRAHYDROTHIOPHENE, 1,1-DIOXIDE



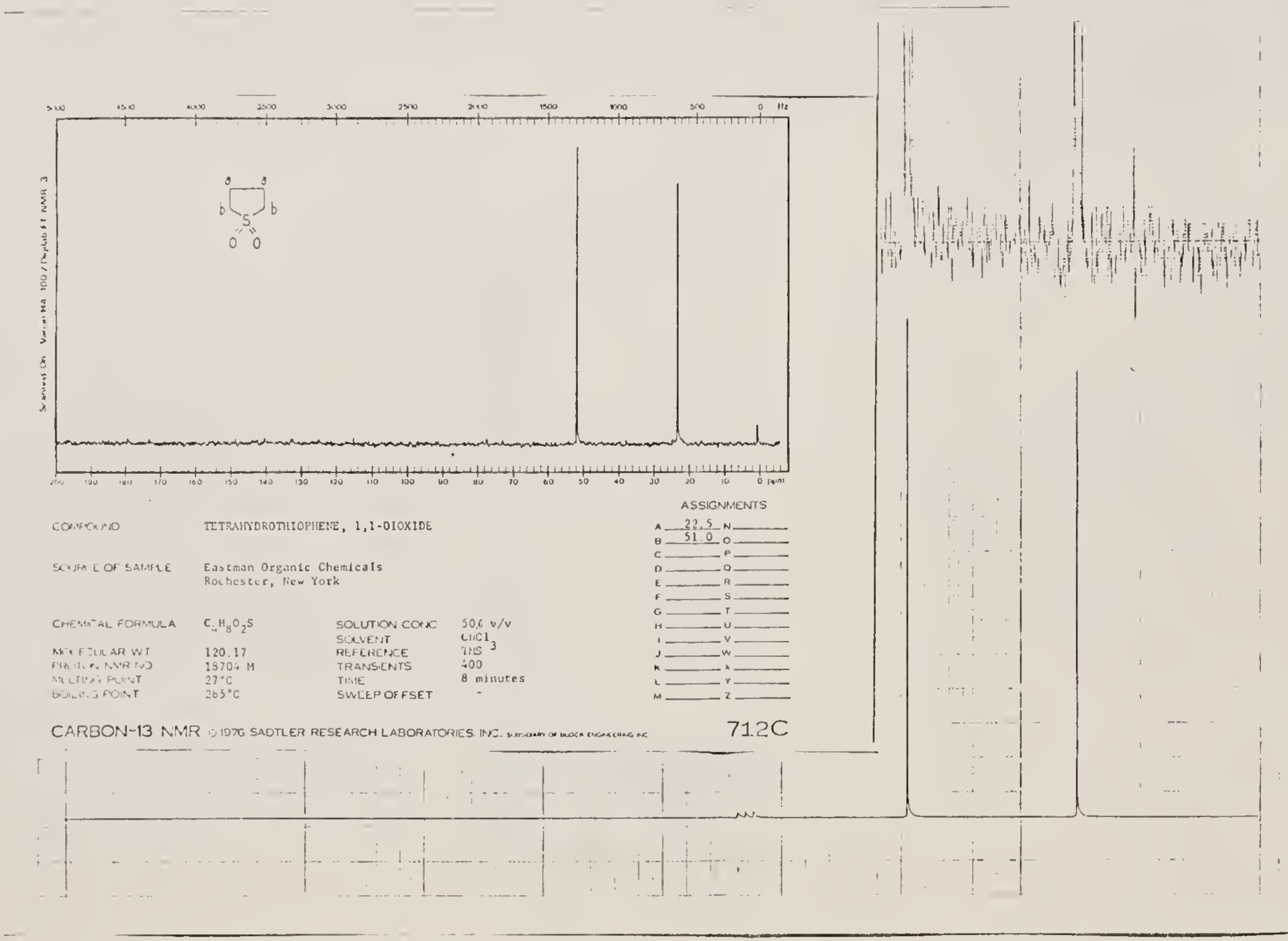
$C_4H_8O_2S$

M.W. 121.07
M.P. 27.5°C
B.P. 100-104°C @
1-2mm

Capillary Cell:
Neat

Figure 5

^{13}C NMR spectrogram of sulfolane



COMPOUND TETRAHYDROTHIOPHENE, 1,1-DIOXIDE

SOURCE OF SAMPLE Eastman Organic Chemicals
Rochester, New York

CHEMICAL FORMULA $C_4H_8O_2S$
MOLECULAR WT 120.17
PROTON NMR NO 18704 M
MELTING POINT 27°C
BOILING POINT 265°C

SOLUTION CONC 50.6 v/v
SOLVENT $CHCl_3$
REFERENCE TMS
TRANSIENTS 400
TIME 8 minutes
SWEEP OFFSET -

ASSIGNMENTS

A	22.5	N	
B	51.0	O	
C		P	
D		Q	
E		R	
F		S	
G		T	
H		U	
I		V	
J		W	
K		X	
L		Y	
M		Z	

CARBON-13 NMR © 1976 SADTLER RESEARCH LABORATORIES, INC. SUBSIDIARY OF BLOCK ENGINEERING INC. 712C

Sulfolane

CDCl3
60%
TMS
5

13C 47.00
1H 51.00

10

5
1000
16384
5000
2500
5 .5
14
2.6 2.1

JAN 18 1980
R.K.

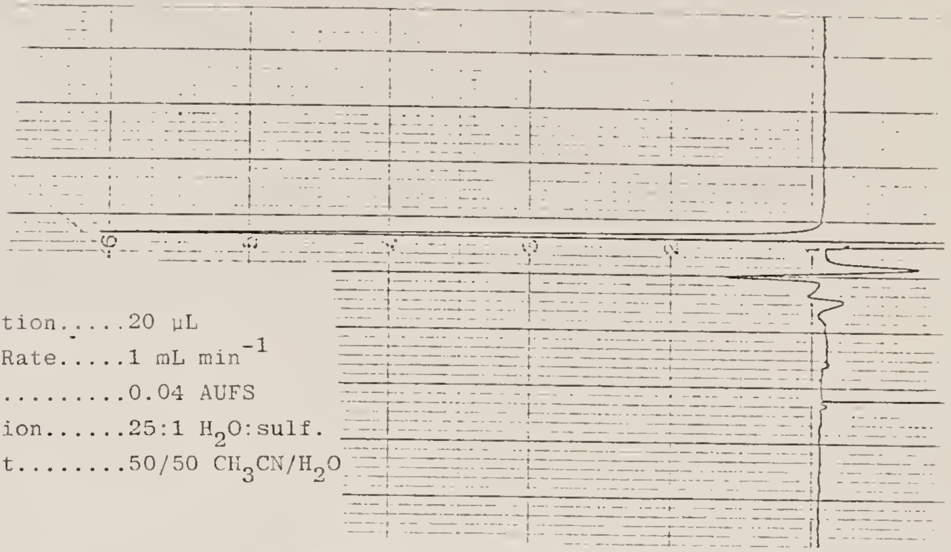
Red curve. x100 }
Blue curve high
field peak
x100 } x10 ←

Figure 6a

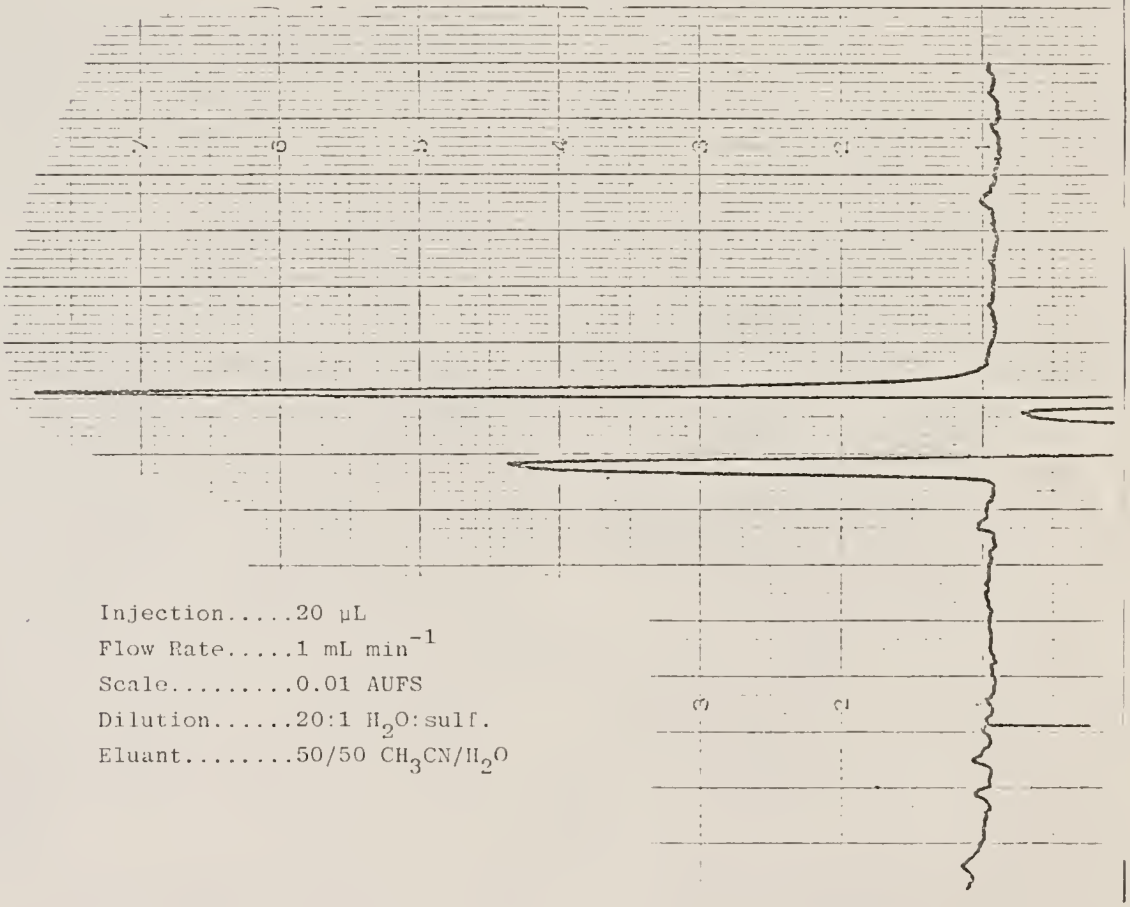
Chromatogram of pure sulfolane
Reverse phase column

Figure 6b

Chromatogram of sulfolane-HCl
Reverse phase column



Injection.....20 µL
Flow Rate.....1 mL min^{-1}
Scale.........0.04 AUFS
Dilution......25:1 H_2O:sulf.
Eluant........50/50 CH_3CN/H_2O



Injection.....20 µL
Flow Rate.....1 mL min^{-1}
Scale.........0.01 AUFS
Dilution......20:1 H_2O:sulf.
Eluant........50/50 CH_3CN/H_2O

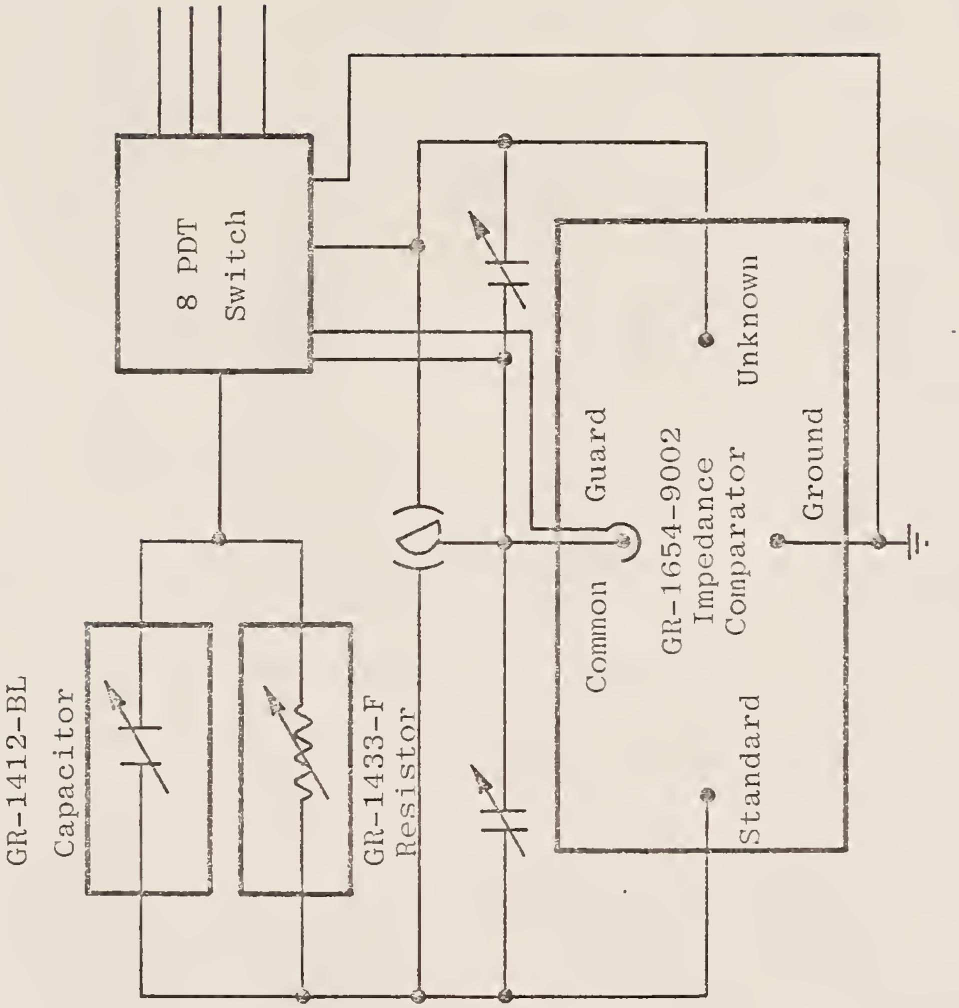
Equipment

The major instrument used in this study was a conductance bridge, in general of a design suggested by Janz and McIntyre.[32] A schematic diagram of the bridge appears in Figure 7. At the heart of the bridge is a General Radio Type 1654-9002 impedance comparator. Originally designed to measure impedance at 0.1, 1.0, 10.0 and 100.0 kHz, the instrument was modified by General Radio to measure at 1.0, 2.5, 5.0, and 10.0 kHz. The instrument utilizes a transformer bridge measurement circuit, with the transformer bridge of toroidal design. The secondary winding of this transformer is center-tapped, and consists of two identical wires, twisted together and wound on the torus. The two halves of this secondary act as the ratio arms of the bridge and are equal to within one part in 10^6. The other two arms of the bridge consist of the unknown impedance (the conductivity cell) and the standards.

The standards used in this instrument are a General Radio Type 1433-F decade resistor and a General Radio Type 1412-BL decade capacitor connected in parallel to the decade resistor. The resistor has seven decades of resistance, with steps of 10 kΩ down to steps of 0.01 Ω. The capacitor has five decades of capacitance, ranging from steps of 0.1 μF down to steps of 1 pF. Using both of these standards, it was possible to measure both the resistance of the test cell, for conductivity, and the capacitance, for dielectric constant measurements. For typical readings, the precision of the standards is 0.01%.

Figure 7

Janz-McIntyre Conductance Bridge


8 PDT
Switch
GR-1412-BL
Capacitor
GR-1433-F
Resistor
Common
Guard
GR-1654-9002
Impedance
Comparator
Unknown
Ground
Standard

The null-point of the bridge was monitored with a Keithley model 191 digital voltmeter. This permitted far more accurate zeroing of the meter (0.001 volt) than visual observation of the meter needle.

To eliminate the problem of irreproducible contact resistances between the bridge circuit and the test cell, and to obviate the necessity of making corrections for lead resistances, the instrument was adapted to utilize a four-lead measurement system. This is the same system utilized with four-lead platinum resistance thermometers[56a,b] and requires two measurements with alternate sets of leads. The mean of the two measurements effectively averages out resistances inherent to the leads and the connections.

To further cut down on problems associated with connection of the cell to the bridge, printed circuit boards and edge connectors were used. Standard equipment with 15 contacts was used, allowing three contacts per lead, with one contact between live connections as a spacer. The multiplicity of contacts per lead insured good and reproducible contact.

The conductance cells used in this study were of the type designed by Daggett, Bair, and Kraus,[36] and were obtained from Beckman Instruments. The constants determined for the cells were 1.05393 and 0.120695 cm^{-1}. The cell appears in Figure 8. The leads are held well separated to help reduce the Parker effect.[24,27] This effect is caused by the electrical leads passing through the electrolyte

Figure 8

Conductance cell

solution, and gives rise to a capacitative effect causing a frequency dependence in the measured resistance.

Another source of error in conductance measurements related to the measuring cell is the Soret effect. This has been discussed in depth by Stokes.[33] Briefly, this effect is due to a slow thermal diffusion of the electrolyte within the electrode compartment. The design of the flask-type dilution cell used in this study, coupled with constant stirring, minimizes this effect.

The electrodes of the cell were shiny platinum, with a circular cross section. They were spot welded to platinum wire, which in turn was welded to tungsten wire to achieve a seal with the glass. Heavy gauge copper wire was welded to the tungsten to form the cell leads, and the copper wire was doubled at the top of the cell to produce the four-lead measurement system.

With two cells in the temperature bath simultaneously, held in close proximity to one another, any shaking could result in mutual damage. For this reason, a special filler cap was designed[57] to facilitate additions to the cell without shaking. The filler cap and its companion weight buret appear in Figure 9. By adjusting the position of the 3-way stopcock, additions could be made, and then solution forced up the fill-tube into the upper chamber. This permitted the washing down of any splashes made during the addition and facilitated solution mixing. Both the weight buret and the filler cap were manufactured by the

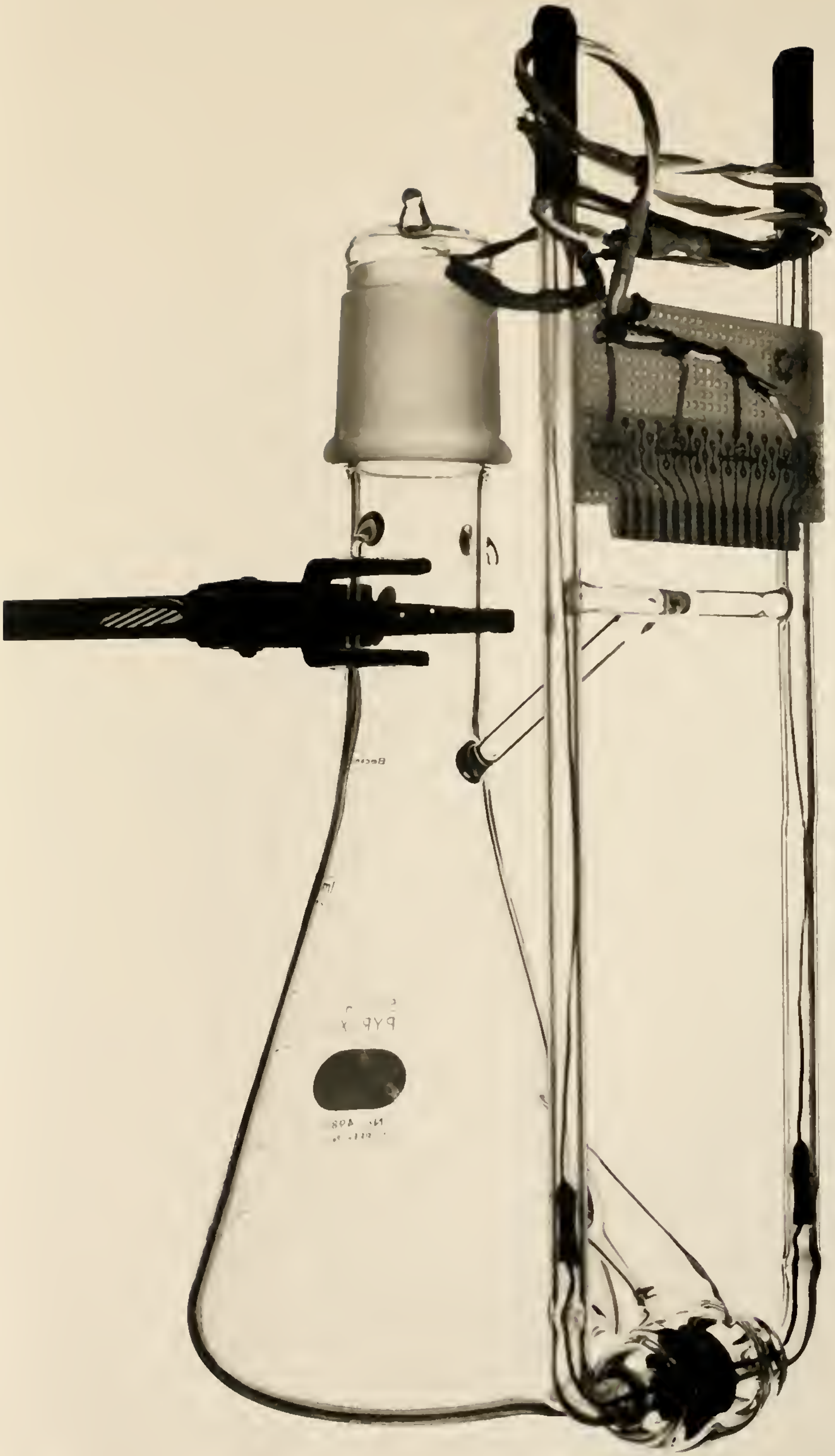
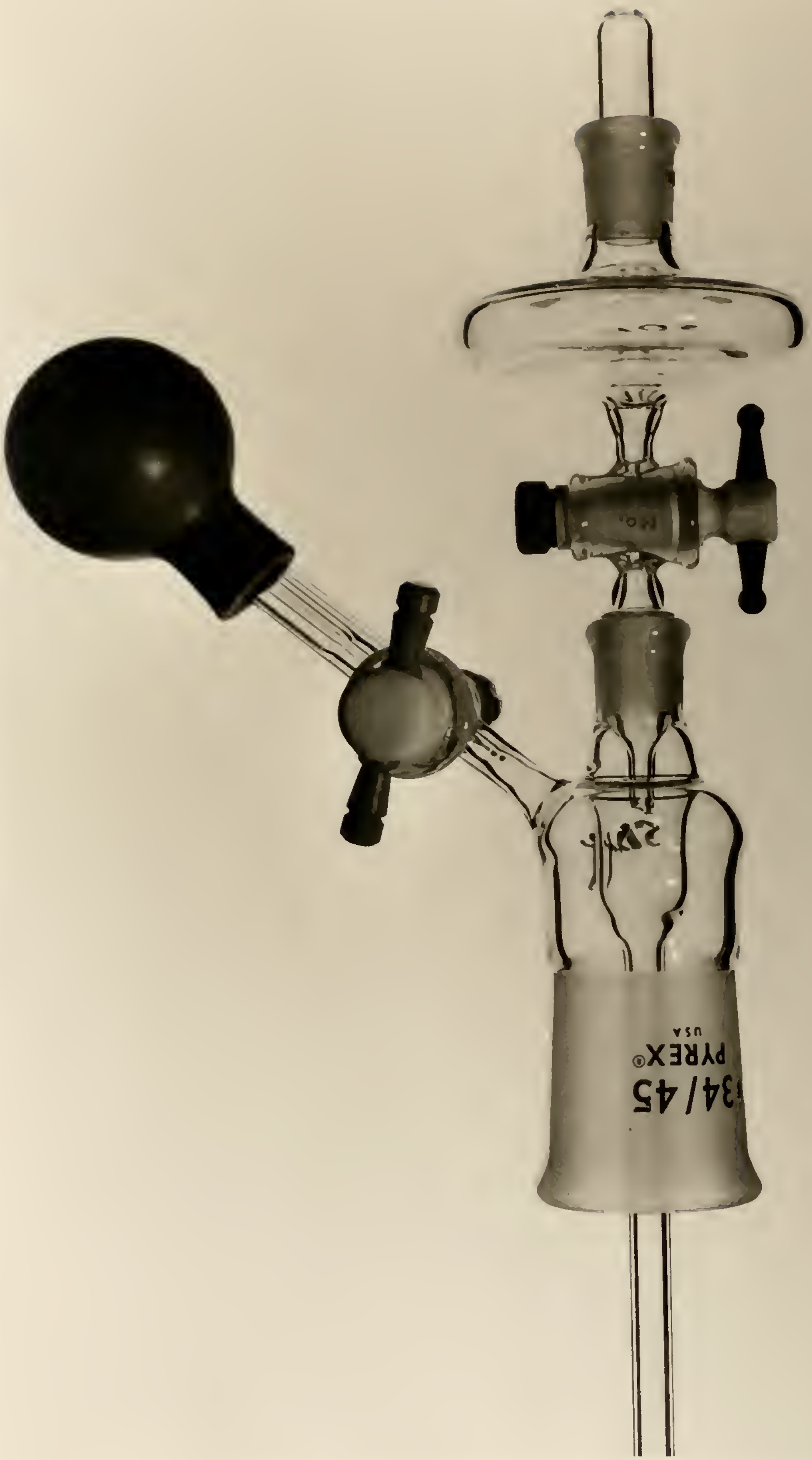


Figure 9

Filler cap and weight buret


34/45
PYREX
USA

departmental glassblower and utilize standard ground-glass joint connections.

The constant-temperature bath utilized in this study was constructed by the departmental machine shop out of stainless steel, with all seams welded. It was insulated with styrofoam and was supported by an aluminum box frame mounted on a welded angle-iron cart. The bath was filled with BP food-grade white oil, which further helped to minimize the Parker effect mentioned previously.[25] The oil was circulated by two American Instrument Company 1.3 A circulating pumps, to assure temperature uniformity throughout the bath.

Temperature control was achieved with a Yellow Springs Instrument Company model 72 proportional temperature controller. The usual three-quarter turn potentiometer used for regulation of fractions-of-a-degree was replaced with a ten-turn potentiometer to provide far more precise control of the temperature setting. The controller was used with a YSI thermistor probe and was used to drive two heaters. One was a standard 500-watt Vycor sheathed immersion heater. The other was constructed of nichrome heating wire wound around a plexiglas frame; it was placed to take full advantage of the flow from the two circulating pumps.

Immersed in the bath were a number of coils of copper tubing. Through these coils was circulated water from an external bath. This bath was cooled by a Blue-M

Constant-Flow model PCC-24A-2 cooling unit, which has thermostatic control. This external water bath was kept approximately 3°C cooler than the temperature of the main bath; as a result, the heaters in the main bath were never completely shut off. This allowed constant regulation of the temperature of the bath rather than the cycling usually associated with proportional temperature controllers. The water from the external bath was circulated by an American Instrument Company 1.3 A circulating pump, and the regulation of temperature in the main bath by the apparatus described above was ±0.002°C.

Temperatures were monitored with a Hewlett-Packard model 2801A digital quartz thermometer and quartz probe. This digital thermometer was calibrated across the entire temperature range of interest, and the appropriate correction factors were determined. It was calibrated against a Leeds and Northrup platinum resistance thermometer, model #8160. The resistance of the resistance thermometer was measured with a Leeds and Northrup type G-2 Müller bridge, model 8069, which allowed measurement of thermometer resistance to 0.0001 Ω. A response printout from Leeds and Northrup permitted the determination of temperature measured directly from the resistance reading.

To further cut down on heat loss from the bath, and to prevent debris from entering the oil, a plexiglas lid for the bath was constructed by the departmental machine shop. This lid had a hinged door over the cell area to allow access to the cells therein.

The cells were stirred constantly by a Poly Science Corporation model RZR-10 stirrer motor, which permitted variable stirrer speed. The motor was connected via a driveshaft and two Sears Craftsman right-angle drives to a Pic chain-and-sprocket drive. This drive turned two large teflon stirbars positioned under the two cells. The temperature bath and its associated components are diagrammed in Figure 10.

Dielectric constants were determined using a Balsbaugh Laboratories model 100-T3 dielectric constant cell. This cell had a three-terminal arrangement and was constructed of cylindrical nickel-steel electrodes. A special wiring harness was constructed to allow connection to the four-lead measuring system of the conductance bridge. The cell was thermostated in the constant temperature bath, and after thermal equilibrium was reached no appreciable drift in capacitance was noted.

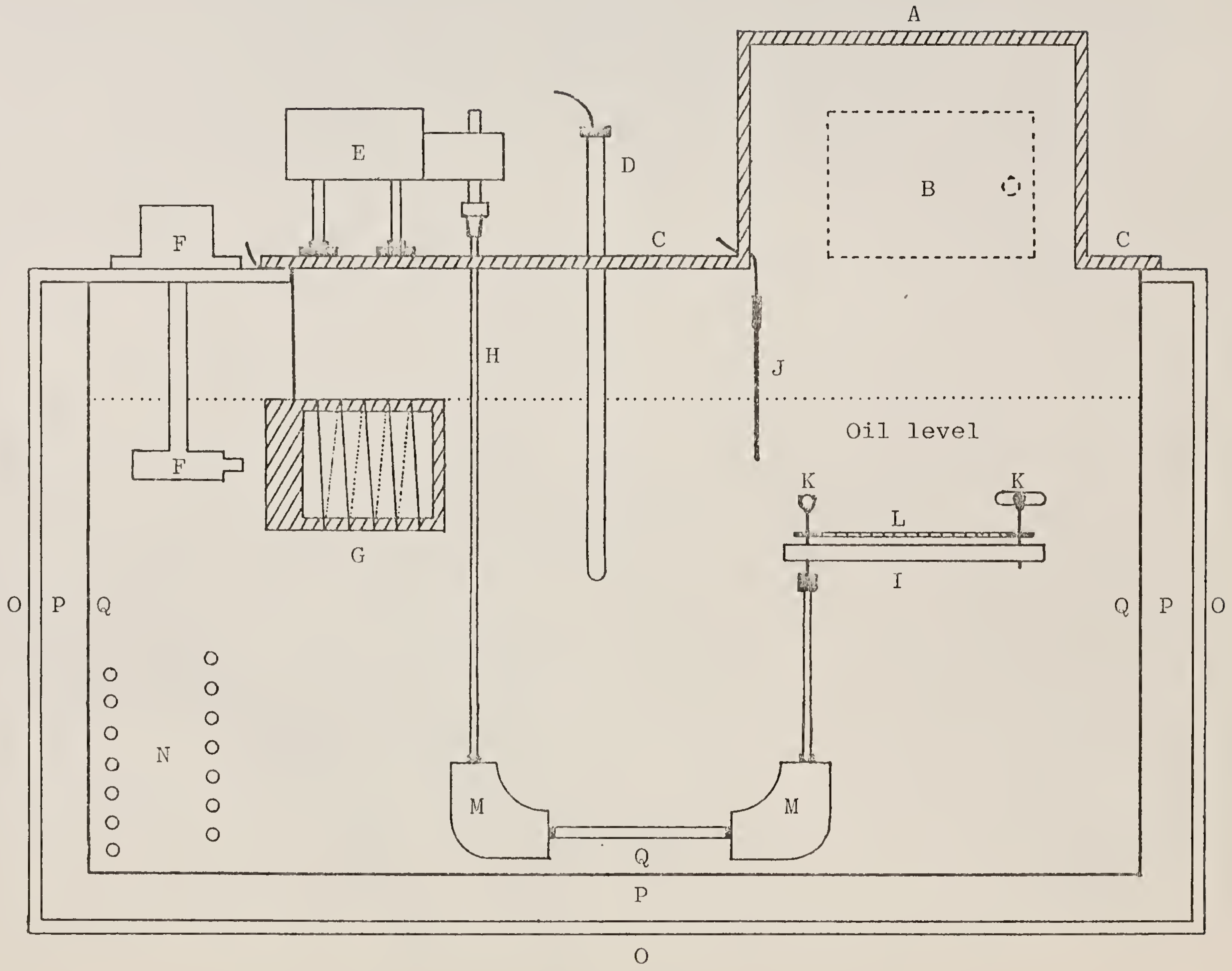
Viscosities were determined with a Canon-Fenske type viscometer, calibrated with conductivity water at the various temperatures studied.

Densities were determined with three pycnometers of the Gay-Lussac type, obtained from the Fisher Scientific Company. The pycnometers were calibrated with conductivity water at the temperatures studied, and the three readings were averaged together to obtain the mean density.

Figure 10. Cross sectional representation of the constant temperature bath and its associated components.

CAPTIONS

A	Access hatch on plexiglas cover.
B	Door in access hatch
C	Plexiglas cover on bath.
D	Standard 500 watt Vycor sheathed heater.
E	Poly Science variable speed stirrer motor.
F	American Instrument Company circulating pump (2).
G	Plexiglas frame wound with nichrome heater wire.
H	Motor drive shaft.
I	Brass bearing support.
J	Thermistor probe for temperature controller.
K	Teflon stirring bar (2).
L	Pic chain-and-sprocket drive.
M	Sears right angel drive (2).
N	Copper coils for cooling water.
O	Aluminum outer wall.
P	Styrofoam insulation.
Q	Stainless steel inner wall.


A
E
D
B
F
C
C
H
J
Oil level
F
K
K
L
G
I
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Q
Q
P
O
N
M
M
Q
P
O

CHAPTER IV

DATA ACQUISITION AND TREATMENT

Experimental Technique

A standard procedure for conductance measurements was adopted and adhered to for this study. An amount of solvent (usually about 350 g) was weighed into the conductance cell, which was then placed into the constant temperature bath. After thermal equilibrium was reached (in about an hour), the resistance of the solvent was measured. Since solvent resistances generally range from 10^5 to 10^6 Ω, and since the decade resistance standard had a maximum resistance of 99,999.99 Ω, it was found necessary to employ a resistive shunt. This shunt, in parallel to the conductance cell, was a precision resistor whose resistance was evaluated on the bridge as 10,006.8 Ω. Response was found to be flat across the frequency range of the measurements. This allowed measurement of the very high resistances according to the equation:

$$R_a = \frac{R_s R_m}{R_s - R_m} \qquad (30)$$

where R_a is the solution resistance, R_m is the measured resistance, and R_s is the shunt resistance.

Once the solvent resistance was determined, the cell, with contents continuously stirred, was allowed to remain undisturbed and the resistance was monitored as a function of time. If the solvent were to leach any impurity out of the glass of the cell, the resistance would decrease with time. This was not noted for any of the solvent systems in this study.

A concentrated solution of the electrolyte under study was prepared in the solvent of interest. Weighed amounts of this stock solution would be added incrementally to the cell via the filler cap. After each addition, the fill tube would be rinsed with the solution in the cell by forcing the solution up into the fill tube with the rubber bulb. After equilibrium was reached, as indicated by stability of the measured resistance with time, the solution resistance was recorded and another addition of stock solution was made. Usually, 12 such solutions were measured, and after the last measurement the density of the final solution was measured.

Resistances were measured with a test voltage of 0.3 V at three frequencies: 2.5, 5.0, and 10.0 kHz. These resistances were then extrapolated vs. a function of frequency to eliminate the frequency dependence, as described in a following section.

Solution equilibrium, for the 2-methoxyethanol/water solvent system, was found to be attained in about 15 minutes. For the sulfolane/water system, equilibrium took up to one hour, probably due to the very slow solvation of the cation by the solvent. For the 1-methyl-2-pyrrolidinone/water system, equilibrium was achieved in about 15 minutes. Quickest of all was the system of Tris·HCl in water, with equilibrium in less than 5 minutes.

Making the conductance measurements in the manner described above gave rise to a set of concentration (in moles of solute per gram of solution) vs. resistance points. Treatment of these data is described in a following section.

Dielectric constant measurements were greatly facilitated by the use of a three-terminal dielectric constant cell. The bridge was balanced (shunt in place) with the cell disconnected. With the cell connected, the capacitance of the empty cell (i.e., with air as the dielectric medium) was measured. The cell holder was then filled with the solvent of interest and placed into the constant temperature bath. The cell was inserted, and the solution was allowed to come to thermal equilibrium. The capacitance was then measured, and the dielectric constant was very simply calculated with the equation:[58]

$$\varepsilon = \frac{C_s}{C_a} \tag{31}$$

where C_s is the solvent capacitance and C_a is the capacitance of the empty cell.

Cell constants were determined utilizing the method described by Lind, Zwolenik, and Fuoss.[59] Utilizing data available for the conductance of aqueous potassium chloride, they derived an equation to give the equivalent conductance, Λ, for a given concentration of KCl:

$$\Lambda = 149.93 - 84.65\sqrt{c} + 58.74c \log c + 198.4c \qquad (32)$$

where c is the molar concentration of KCl. They found this equation to give excellent results when compared to the Jones and Bradshaw[26] conductance standard, probably the most widely accepted standard for conductance measurements.

The method was utilized by making a conductance run using water as the solvent and adding increments of a concentrated KCl stock solution. Once the concentrations were converted to molarity and the resistances extrapolated to remove frequency dependence, the cell constants were calculated.

As was shown in a previous chapter, the resistance of a solution is directly relatable to the specific conductance:

$$\kappa = \frac{\theta}{R_s} \qquad (33)$$

The solution resistance is the measured resistance, after extrapolation, corrected for the resistance of the solvents:

$$\frac{1}{R_s} = \frac{1}{R_m} - \frac{1}{R_{solv}} \qquad (34)$$

The specific conductance may also be related to the equivalent conductance:

$$\kappa = \frac{\Lambda c}{1000} \qquad (35)$$

Combining equations 33 and 35 we obtain an expression relating cell constant, solution resistance and equivalent conductance:

$$\Lambda = \frac{1000\theta}{R_s c} \qquad (36)$$

where c is the concentration in mol L^{-1}.

By plotting Λ, calculated with equation 32, vs. the quantity $(R_s c)^{-1}$, a line is obtained whose slope is 1000θ.

In this study, two separate calibration runs were made, with a total of 10 measurements for each of the two conductance cells. The cell constants were determined by linear regression analysis to be 1.05393 cm^{-1} and 0.120695 cm^{-1}. In both cases, the correlation coefficient for the regression was greater than 0.99999, indicating extremely good reproducibility between runs.

Recently, an alternate equation for the determination of the equivalent conductance of potassium chloride solutions has been proposed by Justice.[60] His equation has the form:

$$\Lambda = 149.87 - 94.87\sqrt{c} + 58.63c \log c + 224.1c - 254.5c^{1.5} \qquad (37)$$

It can be seen that this equation has a similar form to the equation of Fuoss et al. but is extended to include the $c^{1.5}$ term. By doing so, the applicability of the equation is extended up to approximately 0.04 M KCl, as opposed to 0.012 M KCl for the Fuoss equation.

A more recent paper by Fuoss and Hsia[44] contains a modification of the original equation which incorporates the $c^{1.5}$ term:

$$\Lambda = 149.936 - 94.88\sqrt{c} + 25.48c \ln c + 221.0c - 299c^{1.5} \quad (38)$$

As can be seen, the constants differ slightly from the equation proposed by Justice. It is stated that the new Fuoss equation will provide agreement with the Jones and Bradshaw 0.1 demal KCl standard, thus extending the concentration range over which the cell can be calibrated.

Since this study, however, was done at concentrations on the order of 0.01 M maximum, the original Fuoss equation was used for the determination of the cell constants. At such low concentrations, the difference between the Λ values generated by that equation and the values generated by the two later equations is less than one-half of one percent.

Preliminary Data Treatment

As has been mentioned previously, concentrations were determined by weight, and solution additions were by weight. This resulted in experimental concentrations in units of mol g soln^{-1}. Since equivalent conductance is in terms of molarity, it was necessary to convert to molar concentrations. This was done through use of the density of the solution.

Both the solvent density and the density of the final most concentrated conductance solution were determined. The densities of the more dilute solutions were assumed to lie on a straight line connecting the two experimental points. The concentration in mol g soln^{-1} and the molar concentration may be related by the equation:

$$c(M) = 1000m(\rho_{sl}m + \rho_{soln}) \qquad (39)$$

where m is the concentration in mol g soln^{-1}, ρ_{sl} is the slope of the line connecting the two experimental densities, and ρ_{solv} is the solvent density. The quantity $\rho_{sl}m + \rho_{solv}$ is in fact the density of the solution whose concentration is m.

Resistances were measured at 2.5, 5.0, and 10.0 kHz and were then extrapolated to infinite frequency by use of the method endorsed by Hoover for shiny platinum electrodes such as were used in this study.[35] The extrapolation is based on an equation of the form:

$$R_{measured} = R_{ohmic} + \frac{R_2}{1 + a\omega^2} \qquad (40)$$

where:

$$a = \frac{F - 1}{\omega_3^2 - F\omega_2^2}$$

and:

$$F = \frac{\omega_1^2 - \omega_3^2}{\omega_1^2 - \omega_2^2} \cdot \frac{R_2 - R_1}{R_3 - R_1}$$

with $\omega = 2\pi\nu$. At infinite frequency, the term on the right-hand side of equation 40 drops out, leaving the true ohmic resistance. The measured resistance is plotted vs. $(1 + a\omega^2)^{-1}$; the intercept is the ohmic resistance.

Usually, the measured resistance was found to decrease with increasing frequency, which is considered normal. However, when dealing with very high resistances, such as those associated with pure solvents, a reversal of this trend was noted; the resistance increased with frequency. This phenomenon has been described by Mysels et al.[61] and is attributed to a leakage to ground. Their recommendation is that the resistance be extrapolated to zero frequency vs. ω^2. However, their recommendations are for frequencies of measurement less than 0.5 kHz, far lower than those employed in this study.

Where the resistances were found to be sufficiently high to cause anomalous frequency dependence (pure solvents, HCl in sulfolane, acetic acid in 2-methoxyethanol/water) the resistance values at 10 kHz were used for further calculation of conductance parameters.

The preliminary data treatment to this point was performed with a single computer program, called "FREQEXTR," written in the Level II Basic language to utilize a Radio Shack TRS-80 microcomputer, operating under the NewDos+ disk operating system, with 32 KBytes of random access memory (RAM). A copy of the program appears in the Appendix. After inputting the various parameters (density slope, solvent density, cell constant) the resistances and the corresponding frequencies were input, along with the experimental concentration. The computer supplied:

1) The resistance at infinite frequency;

2) The concentration in mol L^{-1}; and

3) The equivalent conductance, calculated via equation 36.

Solvent corrections were always applied.

Treatment of the experimental data with this program yielded a set of molar concentration vs. equivalent conductance data points which were then processed as described below.

Data Processing

The conductance vs. concentration data were processed with a computer program designed to utilize the full Pitts equation described previously. The program was initially written in the Fortran IV language to utilize the facilities of the Northeast Regional Data Center on the campus of the University of Florida.[62] With the acquisition of the microcomputer system described previously, the program was translated into the Basic language; at the same time, the program was streamlined and rendered more efficient. The Fortran IV subroutine "EXPI" for the evaluation of exponential integrals was translated in full. All calculations were carried out in double precision.

The program is designed to utilize an iterative procedure devised by Ives,[63,64] using the following expression for the dissociation constant, K_d:

$$K_d = \frac{c_i^{\,2} y_{\pm}^{\,2}}{c_u} \qquad (41)$$

where the subscripts i and u refer to ionic and nondissociated quantities, respectively. Since the degree of dissociation, α, may be expressed as:

$$\alpha = \frac{\Lambda}{\Lambda_i} = \frac{c_i}{c} \qquad (42)$$

both c_i and c_u may be expressed in terms of total concentration of electrolyte and the degree of dissociation:

$$c_i = \alpha c \qquad c_u = (1 - \alpha)c \tag{43}$$

Combining the preceding four equations, one arrives at an expression for K_d in terms of Λ:

$$K_d = \frac{\Lambda^2 c y_\pm{}^2}{\Lambda_i(\Lambda_i - \Lambda)} \tag{44}$$

In general, Λ_i, the ionic equivalent molar conductance, may be expressed as a function of Λ^o, the limiting equivalent conductance:

$$\Lambda_i = \Lambda^o + \Lambda_r \tag{45}$$

where Λ_r is an expression for altering Λ^o to obtain Λ_i; Λ_r will vary with the theory being applied.

K_d may now be expressed as:

$$K_d = \frac{\Lambda^2 c y_\pm{}^2}{\Lambda_i(\Lambda^o + \Lambda_r) - \Lambda} \tag{46}$$

or:

$$\Lambda - \Lambda_r = \Lambda^o - \frac{\Lambda^2 c y_\pm{}^2}{\Lambda_i K_d} \tag{47}$$

If we now set up two variables, X and Y, such that:

$$Y = \Lambda - \Lambda_r \qquad X = \frac{\Lambda^2 c y_\pm{}^2}{\Lambda_i} \tag{48}$$

we may reduce the equation to the form:

$$Y = \Lambda^o - \frac{X}{K_d} \tag{49}$$

With both X and Y known, this reduces to a simple linear least-squares procedure for obtaining Λ^o (the intercept), and K_d $(-\text{slope})^{-1}$. Since X and Y depend on Λ^o, Ives proposed an iterative procedure whereby an estimate for Λ^o is provided. A set of X and Y values is compiled using this estimate, a least-squares calculation is done, and a new value for Λ^o is obtained. This is then used to generate new values for X and Y, and so forth, until no change in Λ^o is noted. This usually takes less than five iterative steps.

In his original treatment, Ives used the Onsager limiting law to obtain Λ_i; an exact solution for this quantity can thus be obtained. When using the Pitts theory of conductance, however, this is not the case. From Equation 45:

$$\Lambda_i = \Lambda^o + \Lambda_r \tag{45}$$

In the Pitts equation, Λ_r is a transcendental function of Λ_i and a direct solution is not possible. Hence, the program was designed to iterate to obtain the Λ_r value.

The program is designed to take the estimate of Λ^o as the first approximation of Λ_i. It then calculates the various parameters needed (α, c_i, Pitts terms, etc.) and using these calculates the Pitts Λ_r term. Using this, it calculates Λ_i and compares it to the original estimate. If the difference is greater than 0.001, it takes the new Λ_i value and goes through the iteration process again. This is continued until convergence occurs.

The iterative process described above takes place for each data point; once it is concluded, the X and Y values are generated, and the program proceeds to the next point. When all points have been processed, the program performs the least-squares calculation to obtain the values for Λ^o and K_d. In this study, a slight alteration was made to have the program calculate the association constant K_a $(= \frac{1}{K_d})$, rather than the dissociation constant.

This procedure was carried out for five iterations; values of Λ^o and K_a have usually converged by the fourth. The complex point-by-point iterations repeated five times explain why the microcomputer execution time for this program runs in excess of 3.5 hours for a typical set of conductance data! The performance of the program has been tested and found to yield results in very good agreement with those considered standard.[57]

As mentioned in a previous chapter, the full Pitts equation has been expanded by Fernández-Prini and Prue to give an equation of the familiar form:

$$\Lambda = \Lambda^o - S\sqrt{c} + Ec \log c + J_1 c - J_2 c^{1.5} \qquad (23)$$

During his visit to the laboratory, Dr. Fernández-Prini graciously helped to prepare a computer program designed to utilize this form of the conductance equation, for both the Pitts and Fuoss-Hsia theories. This program was also adapted for use with associated electrolytes by replacing c with αc. Since the conductance due to free ions (the ionic conductance) at concentration αc is given by the following relation:

$$\Lambda = \Lambda_i(\alpha c) - \Lambda y_{\pm}{}^2 K_a \alpha c \qquad (50)$$

derived from equation 26, the final form of the conductance equation for associated electrolytes, combining equations 23 and 50 becomes:

$$\Lambda = \Lambda^o - S\sqrt{\alpha c} + E\alpha c \log \alpha c + J_1 \alpha c - J_2(\alpha c)^{1.5} - K_a \Lambda y_{\pm}{}^2 \alpha c \quad (51)$$

As mentioned earlier, the S and E terms are identical for both theories; the J_1 and J_2 terms differ. The program using this form of equation has several advantages over the program utilizing the full Pitts equation. It can give us the results using both theories; using the least-squares iterative method of Kay[65] it operates in single precision and takes only a few minutes to complete the calculations. However, it has one major disadvantage.

In the course of the study, it was found that the program utilizing the expanded equations broke down for the 2-methoxyethanol/water and 1-methyl-2-pyrrolidinone systems. The similarity here is that both systems have dielectric constants of about 32, and consequently Bjerrum's distance is about 8.7 Å. This means that $\kappa a \simeq 0.45$ at a concentration of 0.01 M, and, as has been pointed out,[40,60,66] in this region the expansions tend to break down. This was manifested by a divergence in Λ^o values rather than the expected convergence.

For this reason, among others, the full Pitts equation program, "PITTSEQN" as described, was used to analyze the data in this study. It might be pointed out that, where the expanded equation program worked, it was quite useful for obtaining a close approximation of Λ^o to use as the estimate for Λ^o in "PITTSEQN"; this cut down initial iteration time. Copies of both computer programs, "PITTSEQN" and "EXPEQNS," in the TRS-80 Level II Basic language, appear in the Appendix.

In both programs it will be noted that when the equivalent conductance is input it is multiplied by the factor 0.999505. This is to convert the conductance in international ohms, as measured, into the absolute ohms which are standard.

For those systems studied, where the solvent conductance was an appreciable fraction of the total conductance (i.e., where the association constant was exceedingly high), neither program was able to perform the extrapolation to infinite dilution. Rather, another program was written to utilize the Shedlovsky-Kay extrapolation method.[42] This was devised for use with data for very weak acids in mixed solvent systems (e.g., acetic acid in methanol-water mixtures), and depends on obtaining an estimate for Λ^o, which cannot be directly obtained from the data. This is done by using the Kohlrausch law of independent migration, and will be discussed in depth in the following section. The program for this extrapolation, "SHEDKAY," may be found in the Appendix.

CHAPTER V

RESULTS

This study may be divided into three main sections: first, an examination of the conductimetric behavior of HCl in sulfolane and sulfolane-water solvents of varying compositions at various temperatures; second, a study of the conductimetric behavior of HCl in 1-methyl-2-pyrrolidinone (NM_2Py) and NM_2Py-water solvents of varying compositions; and third, and examination of the behavior of various electrolytes in the solvent consisting of 80 weight-% 2-methoxyethanol and 20 weight-% water in order to determine the amount of ion pairing present for the electrolytes.

In order to avoid the inclusion of large amounts of data in this chapter, the actual conductance results have been placed in Appendix A, which may be found following Chapter VII of this dissertation.

Table I is a summary of the calculated conductance parameters for HCl in sulfolane and sulfolane-water solvents at 25, 30, and 40°C. The solvent composition is expressed as mole fraction of sulfolane (X_s); Λ^o is the limiting equivalent conductance, K_a is the experimental ion pairing constant, a is the value used for the distance of closest approach parameter in the Pitts conductivity theory, and

TABLE I

Calculated conductance parameters for HCl in sulfolane-water solvents at 25, 30 and 40°C.

Temperature (°C)	Solvent Composition (mole fraction sulfolane)	Λ^o ($S\ cm^2\ mol^{-1}$)	K_a ($mol^{-1}\ L$)	a ($cm \times 10^{-8}$)	$\sigma_{\Lambda-\Lambda_c}$	
25	0.85	12.374	756.14	6.19	0.039	
	0.75	18.929	303.19	5.99	0.121	
	0.50	36.344	20.30	5.36	0.022	a
	0.25	104.295	2.54	4.69	0.056	a
	0.00	426.550	0.06	3.58	0.196	b
	0.00	426.290	0.00	3.58	0.026	c
30	1.00	17.6[d]	4.72×10^6	6.36	-----	
	0.85	12.350	526.52	6.17	0.172	
	0.75	20.194	288.13	5.96	0.154	
	0.50	42.108	27.73	5.38	0.053	
	0.25	115.495	2.37	4.79	0.097	
	0.00	457.860	0.06	3.60	0.194	b
40	1.00	17.6[d]	2.45×10^6	6.40	-----	
	0.85	19.698	1336.2	6.15	0.058	
	0.75	26.806	319.47	5.86	0.093	a
	0.50	49.597	26.26	5.37	0.039	a
	0.25	136.504	4.64	4.69	0.114	
	0.00	520.000	0.09	3.65	0.240	b

a---Reference 67

b---Reference 68

c---References 69, 70

d---Calculated value for dissociated HCl at 30°C (see text)

$\sigma_{\Lambda-\Lambda_c}$ is the standard deviation between the experimental and calculated equivalent conductances.

The distance of closest approach parameter, a, was, in this study, set equal to the Bjerrum critical distance; this is discussed in the following chapter.

Table II presents the calculated conductance parameters for HCl in NM_2Py and NM_2Py-water solvents. The symbols have the same meanings as in Table I.

Table III presents the calculated conductance results for several electrolytes in the 80 W% 2-methoxyethanol-water (80 W% MetOH-H_2O) solvent. These electrolytes were chosen in view of their general importance in acid-base chemistry, and to tie in with other research under way at this laboratory.[71] Furthermore, for a comparative evaluation of the results obtained in 80 W% MetOH-H_2O with those in pure water, the behavior of aqueous solutions of Tris·HCl (tris(hydroxymethyl) aminomethane hydrochloride) was studied.[72] The results of this study are summarized in Table IV.

In this case, various trial values of a were used to obtain a minimum in the standard deviation between the experimental and calculated conductances. The value of a which gave the minimum in $\sigma_{\Lambda-\Lambda_c}$ was that selected for use in generating the conductance parameters listed in Table IV.

TABLE II

Calculated conductance parameters for HCl in NM_2Py-water solvents at 25°C.

Solvent Composition (X_{NM_2Py})	Λ^o ($S\ cm^2\ mol^{-1}$)	K_a ($mol^{-1}\ L$)	a ($cm \times 10^{-8}$)	$\sigma_{\Lambda-\Lambda_c}$
1.00	8.848	161.46	8.74	0.141
0.75	16.206	60.63	7.55	0.081
0.50	25.944	10.40	6.22	0.109
0.33	37.605	0.64	5.36	0.017
0.25	52.890	2.45	4.91	0.144
0.00	426.290	0.00	3.58	0.026 [a]

a---Reference 69

TABLE III

Calculated conductance parameters for electrolytes in 80 W% 2-methoxyethanol-water.

Electrolyte	Λ^o ($S\ cm^2\ mol^{-1}$)	K_a ($mol^{-1}\ L$)	a ($cm \times 10^{-8}$)	$\sigma_{\Lambda-\Lambda_c}$
HCl	52.808	14.81	8.70	0.099
NaCl	31.587	17.73	8.70	0.027
Tris·HCl	26.884	29.46	8.70	0.020
NaAc	25.843	25.45	8.70	0.015
HAc	47.064[a]	1.24×10^8	8.70	-----

a---Calculated value (see text)

TABLE IV

Calculated conductance parameters for Tris·HCl in water.

T (°C)	Λ^o (S cm^2 mol^{-1})	K_a (mol^{-1} L)	a (cm x 10^{-8})	$\sigma_{\Lambda-\Lambda_c}$
25	106.07	1.01	2.60	0.225
37	133.65	0.99	3.75	0.098

CHAPTER VI

DISCUSSION

Solvent Properties

General

In general, electrolytic conductance will depend, to a large degree, on the properties of the solvent. If the solvent is able to solvate strongly the ions present, this will aid the dissociation process and increase the conductance of the solution.

There are two basic types of electrolytes.[39] In the first, the ions are already present, as in inorganic salts, and dissociate when dissolved. In the second type, ions are formed by reaction between the solvent and the solute; for example, the reaction which takes place when an organic acid is dissolved in water:

$$\mathrm{RCOOH} + \mathrm{H_2O} \rightleftarrows \mathrm{RCOO^-} + \mathrm{H_3O^+} \tag{52}$$

The most obvious force between a neutral solvent molecule and an ion is the electrostatic force arising from the interaction of the charge on the ion with the permanent dipole moment of the molecule. If the solvent molecule has no permanent dipole moment, one may be induced by the presence nearby of the charged ion. Of a similar nature are the dispersion, or London forces. These are the forces responsible for the cohesion of molecules lacking charge or dipole moments and are due to random formation of dipoles due to fluctuations in the electron clouds of the molecules.

Aside from these non-specific forces, there are several types of specific forces aiding the solvation process. A good example of such is hydrogen bonding. An example is the dissolution of an acid in water, as depicted in equation 52. It is this hydrogen bonding, and the solvent structure that it gives rise to, that leads to the proton jump mechanism which causes abnormally high conductances for strong acids in water. This will be discussed in a later section.

Another of the factors whereby the solvent influences the conductance of an electrolyte therein is the viscosity. Quite obviously, as the viscosity of the solvent increases, the drag on moving ions increases, and the conductance will thus decrease. Yet another factor is the solvent dielectric constant. From Coulomb's Law, it is seen that, as the dielectric constant decreases, the electrostatic forces of attraction increase; thus, the mutual attraction between oppositely charged ions increases, increasing ion association and decreasing conductance.

In view of the above, it is interesting to examine the properties of the solvent systems utilized in this study and to see if any conclusions can be reached concerning solvent properties and conductance.

Sulfolane System

The physical properties of sulfolane and sulfolane-water solvents are summarized in Table V. They are primarily experimental values, supplemented where appropriate by values from the literature.

TABLE V

Physical properties of sulfolane-water solvents.

Temp. (°C)	X_{sulf}	κ (S cm^{-1}) (x 10^{-7})	Density (g mL^{-1})	Viscosity (cP)	Dielectric Constant
25	0.85	0.735	1.2564	7.490	45.23
	0.75	2.658	1.2492	6.772	46.77
	0.50	4.5	1.2290	4.583	52.28 a
	0.25	6.3	1.1726	2.738	59.70 a
	0.00	7.0	0.99707	0.890	78.36 b
30	1.00	1.260	1.2623	10.30	43.30
	0.85	0.298	1.2535	7.236	44.69
	0.75	20.88	1.2464	5.994	46.26
	0.50	2.740	1.2214	3.797	51.25
	0.25	3.610	1.1698	2.287	57.57
	0.00	9.0	0.99567	0.798	76.58 b
40	1.00	0.506	1.2568	7.039	41.68
	0.85	4.388	1.2483	5.240	43.34
	0.75	5.7	1.2353	4.743	45.49 a
	0.50	8.4	1.2082	3.212	49.64 a
	0.25	12.00	1.1579	1.928	56.83
	0.00	10.0	0.99224	0.653	73.15 b

a---Reference 67
b---Reference 73

The values for sulfolane at 30°C are in accord with those found in the literature.[9,10,74] At 40°C, the dielectric constant is in good agreement. The viscosity is found to be somewhat low and the density somewhat high (7.953 cP and 1.2534 g mL^{-1} respectively)[74] compared to the values available from the literature. The experimental values were those used for the calculations.

It can be seen that as the mole fraction of water increases, the viscosity and density decrease and the dielectric constant increases. This is what one would expect. However, the decrease in density with increasing water content is not as great as would be expected were it simply a case of mixing the two components. There, the density would be expected to be the linear combination of the two component densities:

$$\rho = X_s\rho_s + X_w\rho_w \tag{53}$$

where s and w denote sulfolane and water respectively. The density of the solvent mixture vs. mole fraction of sulfolane is plotted in Figure 11a. The deviation from ideality, called the "excess density" is plotted in Figure 11b. This excess density is defined by the equation:

$$\rho_e = \rho_m - (X_s\rho_s + X_w\rho_w) \tag{54}$$

where ρ_m is the measured density.

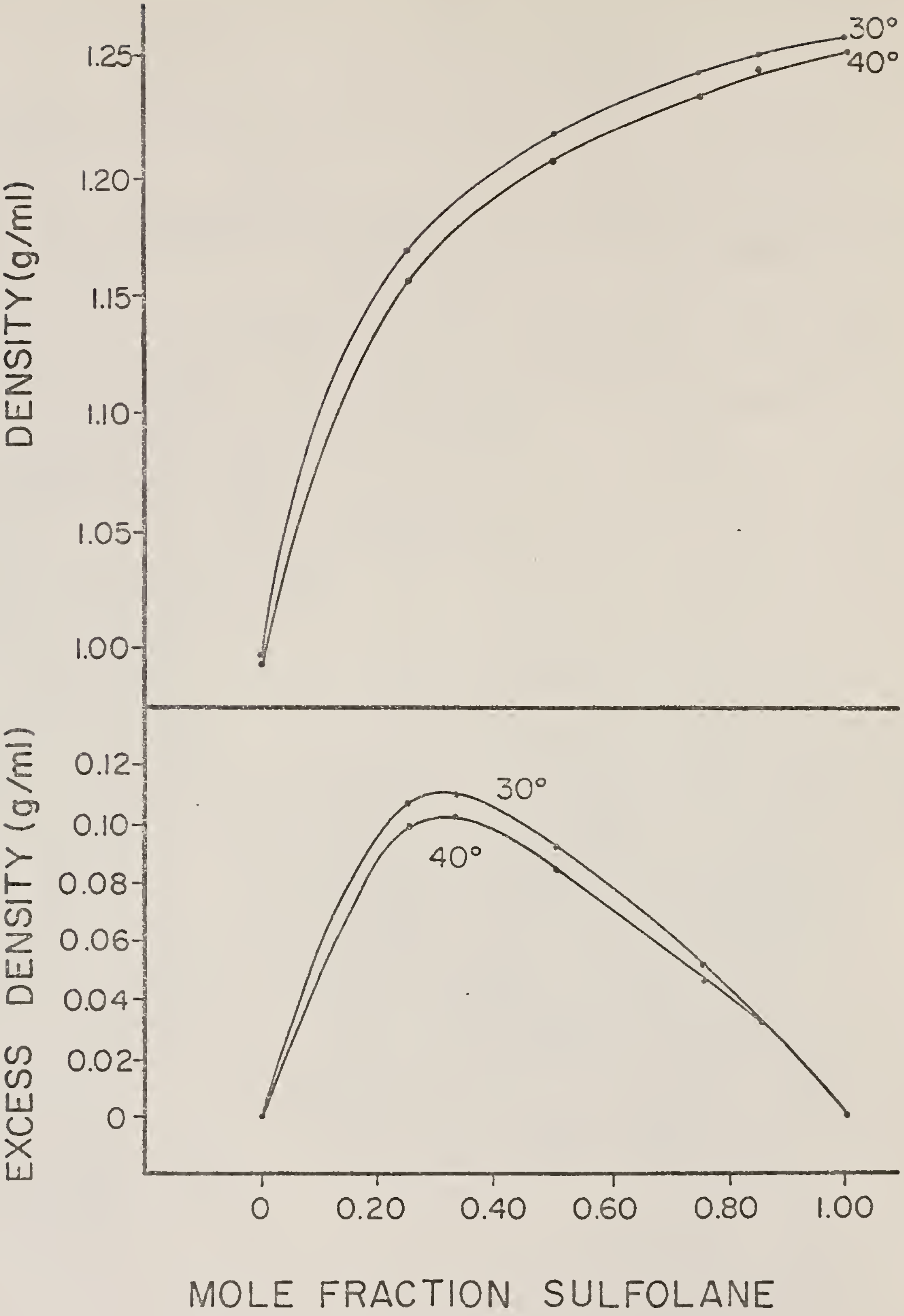
It will be noted that the maximum in the plot of excess density occurs at about 33 mole-% sulfolane, at all of the temperatures measured. The deviation from ideality has been taken to indicate association between the two components of the system.[75] Geddes[76] has indicated that the composition of the system at the point of highest

Figure 11a

A plot of the density of the sulfolane-water solvents vs. the mole fraction of the sulfolane contained therein at various temperatures. The plot for the densities at 25°C is not distinguishable from that for 30°C with the scale employed.

Figure 11b

A plot of the excess density of the sulfolane-water solvents vs. the mole fraction of the sulfolane contained therein at various temperatures. See text for definition of excess density.


DENSITY (g/ml)
1.25
1.20
1.15
1.10
1.05
1.00
30°
40°
EXCESS DENSITY (g/ml)
0.12
0.10
0.08
0.06
0.04
0.02
0
30°
40°
0
0.20
0.40
0.60
0.80
1.00
MOLE FRACTION SULFOLANE

deviation from ideality is that of the associated species. In this case, that would correspond to sulfolane$\cdot$2H_2O.

Figure 12a is a plot of the dielectric constant vs. the mole fraction for the sulfolane-water solvent system. The excess dielectric constant, defined in an analogous manner to the excess density, is plotted in Figure 12b. Here the deviation is negative and again has a maximum deviation at about 33 mole-% sulfolane. This is in accord with the results of Reynaud,[77] and gives further validity to the assumption of an associated species with the composition sulfolane$\cdot$2H_2O.

Figures 13a and 13b are plots of, respectively, the viscosity and excess viscosity of the sulfolane-water solvent system. Here the situation is more confused than in the previous two cases. There is a maximum deviation, but this shifts with the temperature. Although drawing conclusions from this plot is less certain than with the plots of excess density and excess dielectric constant, one thing stands out. The addition of just a small amount of water causes, at 30°C, a drastic decrease in the viscosity of the mixture, indicating a decrease in the structure of the solvent. This is true to a lesser extent at 40°C. It has been shown that sulfolane is an excellent "structure-breaker" with regard to water;[78] apparently the same can be said for water with regard to sulfolane. It has been shown as well that the heat of mixing for sulfolane and water is endothermic; this would correspond to heat being extracted

Figure 12a

A plot of the dielectric constant of the sulfolane-water solvents vs. the mole fraction of sulfolane contained therein at various temperatures. The 25°C plot terminates at X = 0.85 since sulfolane (X = 1.0) is a solid at this temperature.

Figure 12b

A plot of the excess dielectric constant of the sulfolane-water solvents vs. the mole fraction of sulfolane contained therein at various temperatures. See text for definition of excess dielectric constant.

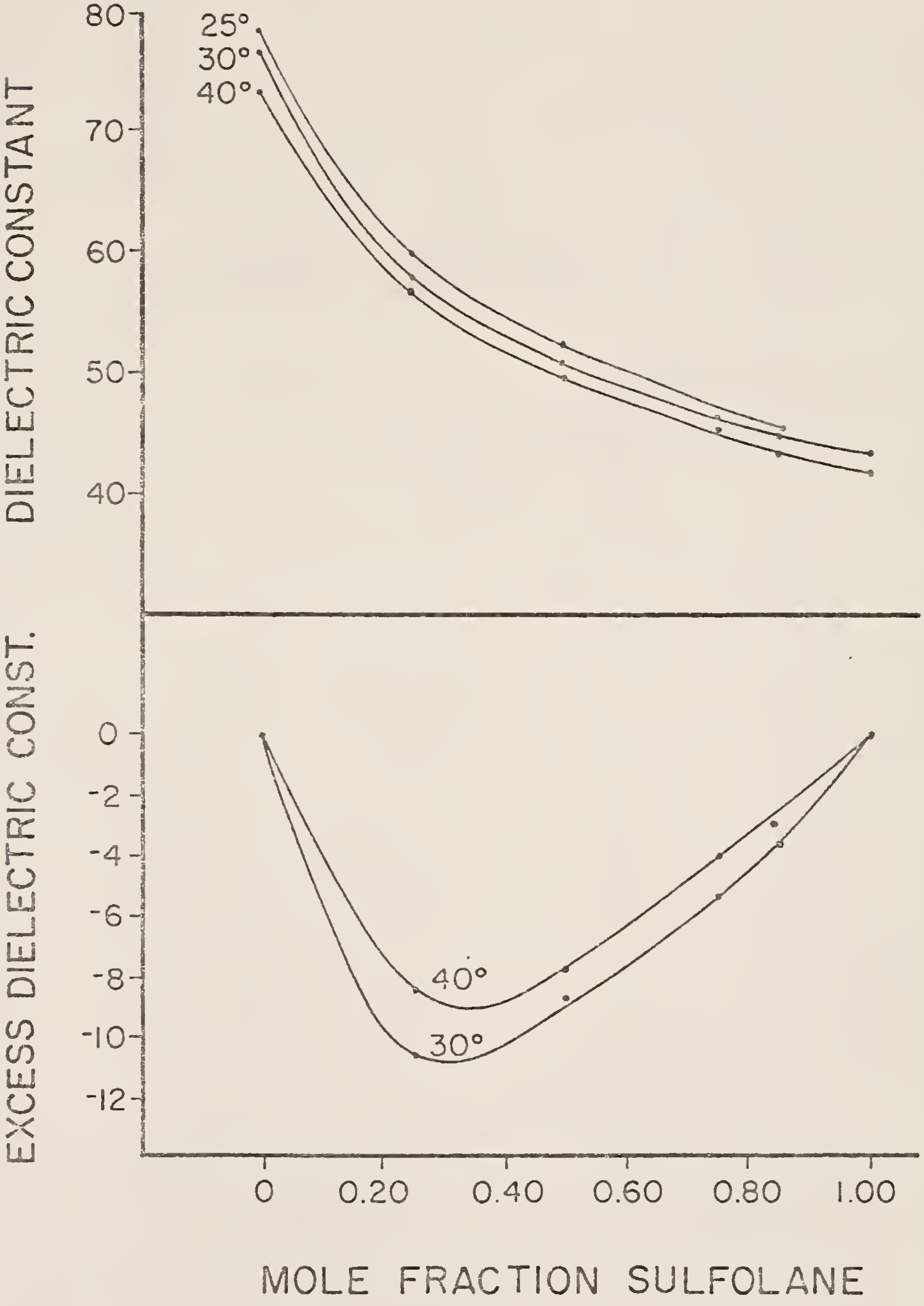
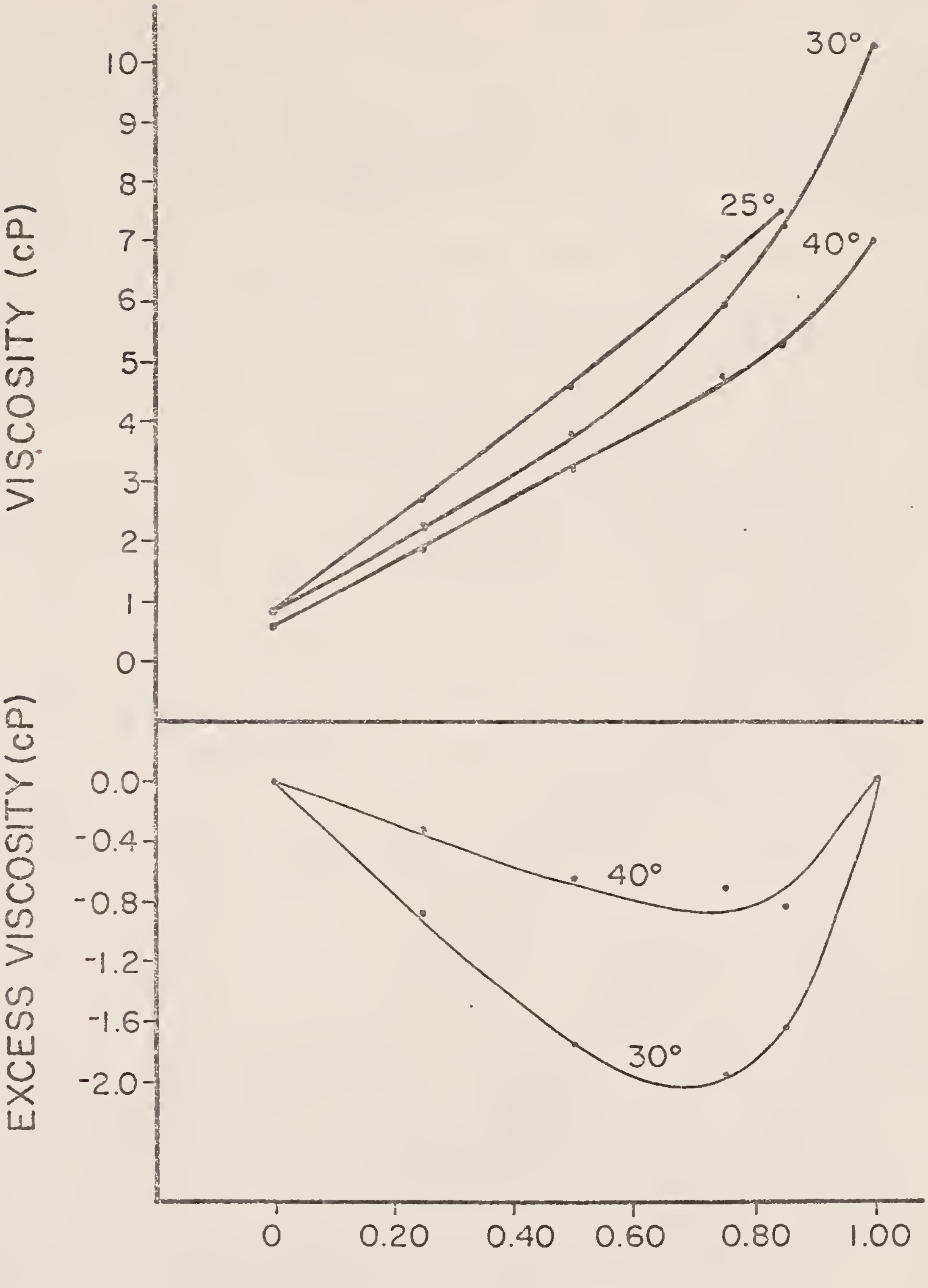

DIELECTRIC CONSTANT
80
70
60
50
40
25°
30°
40°
EXCESS DIELECTRIC CONST.
0
-2
-4
-6
-8
-10
-12
40°
30°
0
0.20
0.40
0.60
0.80
1.00
MOLE FRACTION SULFOLANE

Figure 13a

A plot of the viscosity of the sulfolane-water solvents vs. the mole fraction of the sulfolane contained therein at various temperatures. The 25°C plot terminates at X = 0.85 since sulfolane (X = 1.0) is a solid at this temperature.

Figure 13b

A plot of the excess viscosity of the sulfolane-water solvents vs. the mole fraction of the sulfolane contained therein at various temperatures. See text for definition of excess viscosity.



MOLE FRACTION SULFOLANE

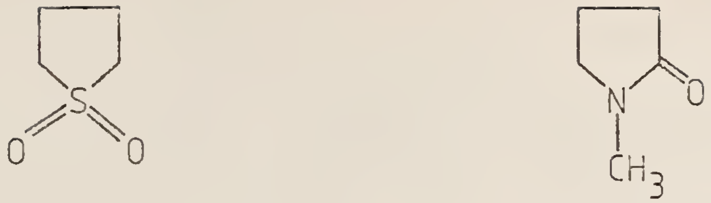
from the solution to break the hydrogen-bonded water structure. As will be shown in the next section, this is significant. It indicates that while there is interaction between the sulfolane and water, it is a structure-breaking process. For other dipolar-aprotic solvents, such as NM_2Py which is discussed next, just the reverse is true.

Pure sulfolane is a somewhat inconvenient solvent to work with. Since it melts at 28.5°C,[9] most work has been done at 30°C, the first even temperature at which sulfolane is a liquid. However, the drastic decrease in viscosity with temperature (drastic when compared to sulfolane-water solvents) seems to indicate that, at 30°C, the sulfolane still retains a great deal of the structure that it had as a solid. This will be explored further when the conductance results are discussed.

NM_2Py System

1-Methyl-2-pyrrolidinone (also N-methyl-2-pyrrolidinone, abbreviated as NM_2Py herein) is a dipolar aprotic solvent similar in many respects to sulfolane. Both solvents have five member heterocyclic ring structures; both have double-bonded oxygens. The structures appear in Figure 14.

The physical properties of NM_2Py and NM_2Py-water solvents are summarized in Table VI. For the most part, these are experimental values, supplemented with literature values where appropriate.



Sulfolane

NM_2Py

Figure 14

Structures of sulfolane and NM_2Py.

TABLE VI

Physical properties of NM_2Py-water solvents at 25°C.

X_{NM_2Py}	κ (S cm^{-1}) (x 10^{-7})	Density (g mL^{-1})	Viscosity (cP)	Dielectric Constant
1.00	3.637	1.0277	1.648	32.06
0.75	7.759	1.0348	2.269	37.12
0.50	13.86	1.0432	3.711	45.01
0.33	28.39	1.0477	5.000	52.25
0.25	12.12	1.0451	4.843	57.00
0.00	7.0	0.99707	0.890	78.36 a

a---Reference 73

The experimental values for the physical properties of pure NM_2Py are in excellent agreement with those reported in the literature.[77,79]

It can be seen that, as the mole fraction of water present in the solvent increases, both the density and the viscosity increase and eventually pass through a maximum at 33 mole-% NM_2Py. Figure 15a is a plot of the density vs. the mole fraction of NM_2Py for this solvent system, while

Figure 15a

A plot of the density of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.

Figure 15b

A plot of the excess density of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.

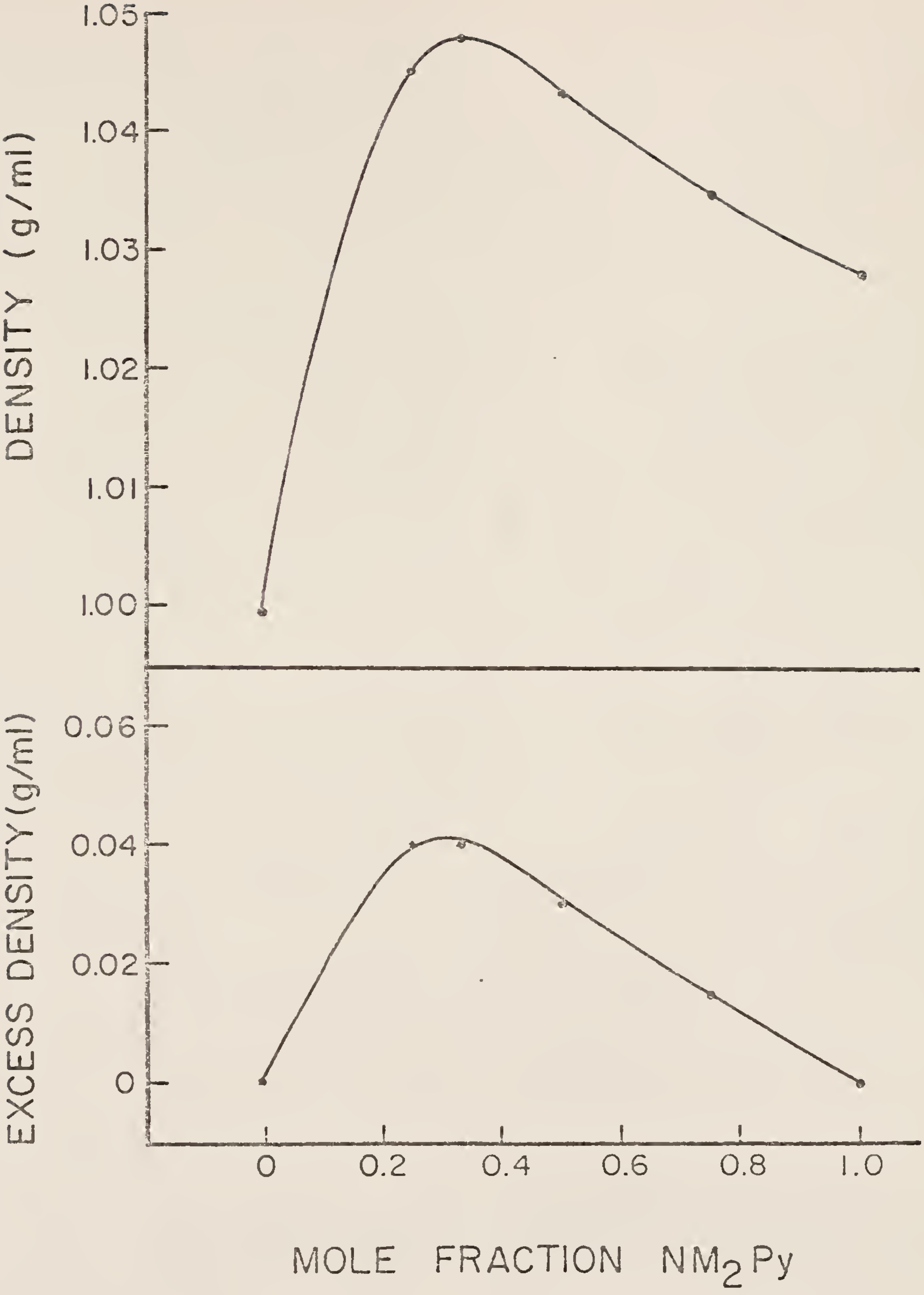

1.05
1.04
1.03
1.02
1.01
1.00
DENSITY (g/ml)
0.06
0.04
0.02
0
EXCESS DENSITY (g/ml)
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NM$_2$Py

Figure 15b is a plot of the excess density, as previously defined. Figures 16a and 16b are, respectively, plots of the viscosity and excess viscosity for these systems. Both excess functions pass through a sharp maximum at 33 M% NM_2Py, indicating a structure for the associated species of $NM_2Py \cdot 2H_2O$, analogous to that found for the sulfolane systems. As can be seen in Figures 17a and 17b (plots of, respectively, the dielectric constant and the excess dielectric constant), this excess function also reaches a maximum value at 33 M%. This finding is in accord with the density and viscosity results, and with the results of Assarson and Eirich,[13] who demonstrated through heat of mixing and phase diagram studies the formation of the aforementioned species $NM_2Py \cdot 2H_2O$. Therefore, it is believed that these results for the dielectric constants must supersede those reported by Reynaud,[77] who showed a maximum for the excess dielectric constant at $X_{NM_2Py} = 0.2$, corresponding to the species $NM_2Py \cdot 4H_2O$.

Although the species formed.apparently have the same stoichiometry, the associative processes for NM_2Py-H_2O and sulfolane-H_2O must be quite different. As was mentioned in the previous section, it is believed that the association of sulfolane with water is a structure-breaking process. When mixing NM_2Py and water, it was quite evident that the solution became warm. It has been reported[78] that the heat of solution of NM_2Py in water is highly exothermic,

Figure 16a

A plot of the viscosity of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.

Figure 16b

A plot of the excess viscosity of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.

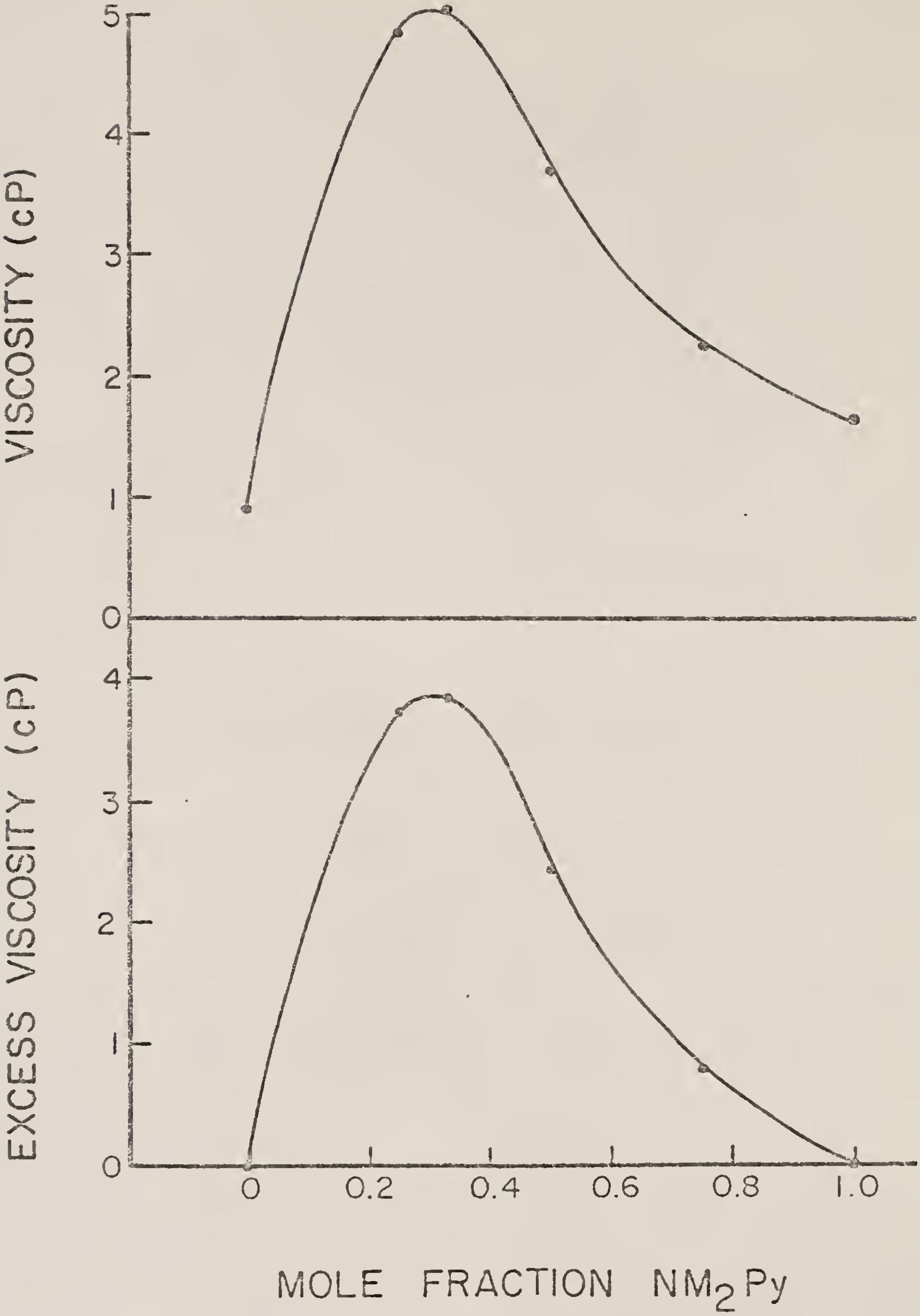
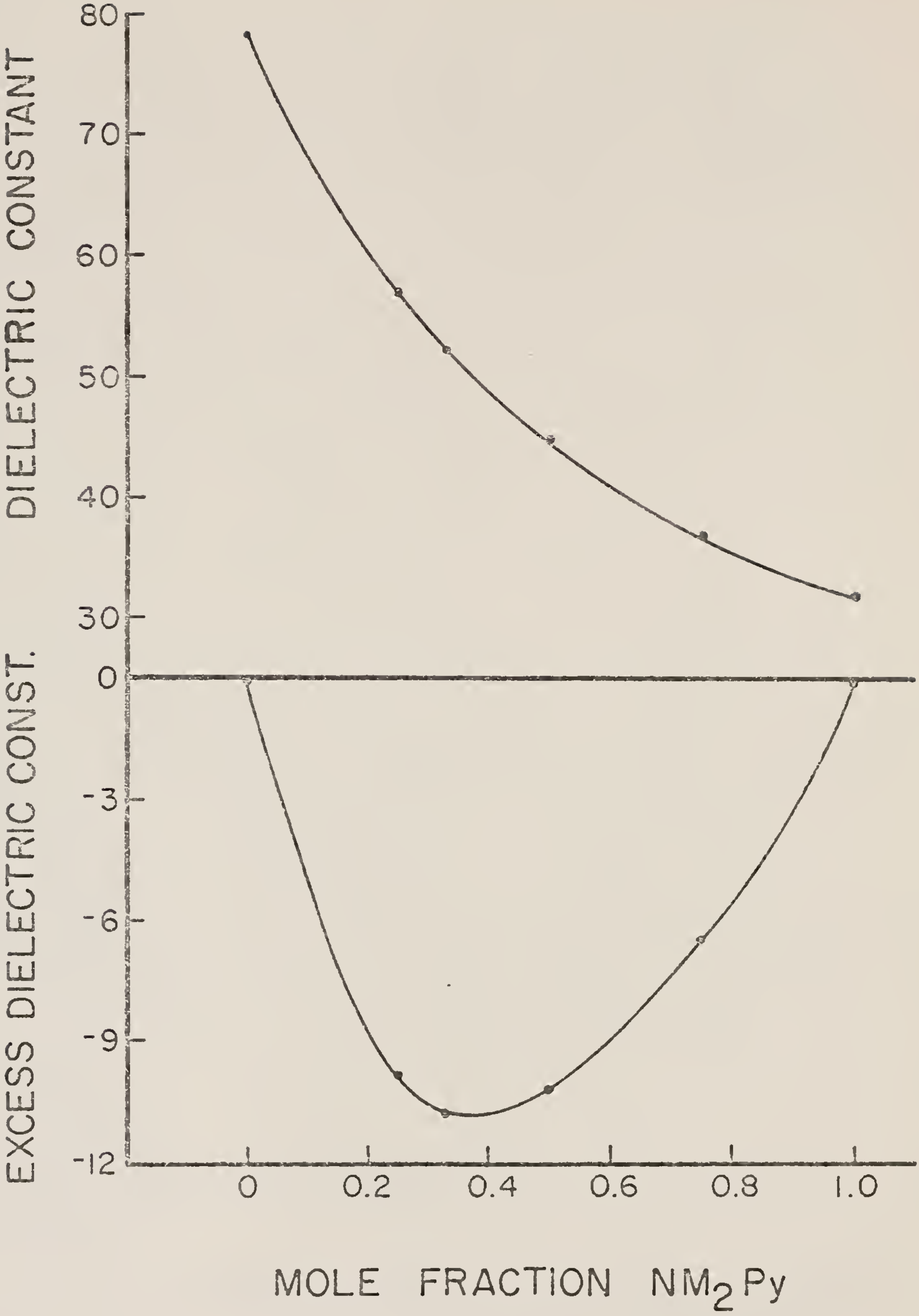

VISCOSITY (cP)
5
4
3
2
1
0
EXCESS VISCOSITY (cP)
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NM2Py

Figure 17a

A plot of the dielectric constant of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.

Figure 17b

A plot of the excess dielectric constant of the NM_2Py-water solvents vs. the mole fraction of NM_2Py contained therein at 25°C.


DIELECTRIC CONSTANT
80
70
60
50
40
30
EXCESS DIELECTRIC CONST.
0
-3
-6
-9
-12
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NM$_2$Py

consistent with the empirical observation. This, coupled with the large increase in solution viscosity, makes it evident that the association between NM_2Py and water is a structure-making process, probably involving hydrogen bonding at the carbonyl oxygen.

Pure NM_2Py has been shown to exist primarily as a monomer.[80] As is evident from the viscosity curve, addition of small amounts of water causes a tremendous increase in the structure of the solvent, indicating a greater tendency for the NM_2Py to associate with water rather than itself. The effect of the various solvent properties which have been discussed, such as association between the two components of the mixture, is discussed in a following section of this chapter.

Conductance Curves

When conductance data are presented graphically it is customary to plot the equivalent conductance, Λ, vs. the square root of the concentration. For a dilute solution of a completely dissociated electrolyte, this would have a form very close to the Debye-Hückel-Onsager equation,

$$\Lambda = \Lambda^o - Sc^{\frac{1}{2}} \qquad (21)$$

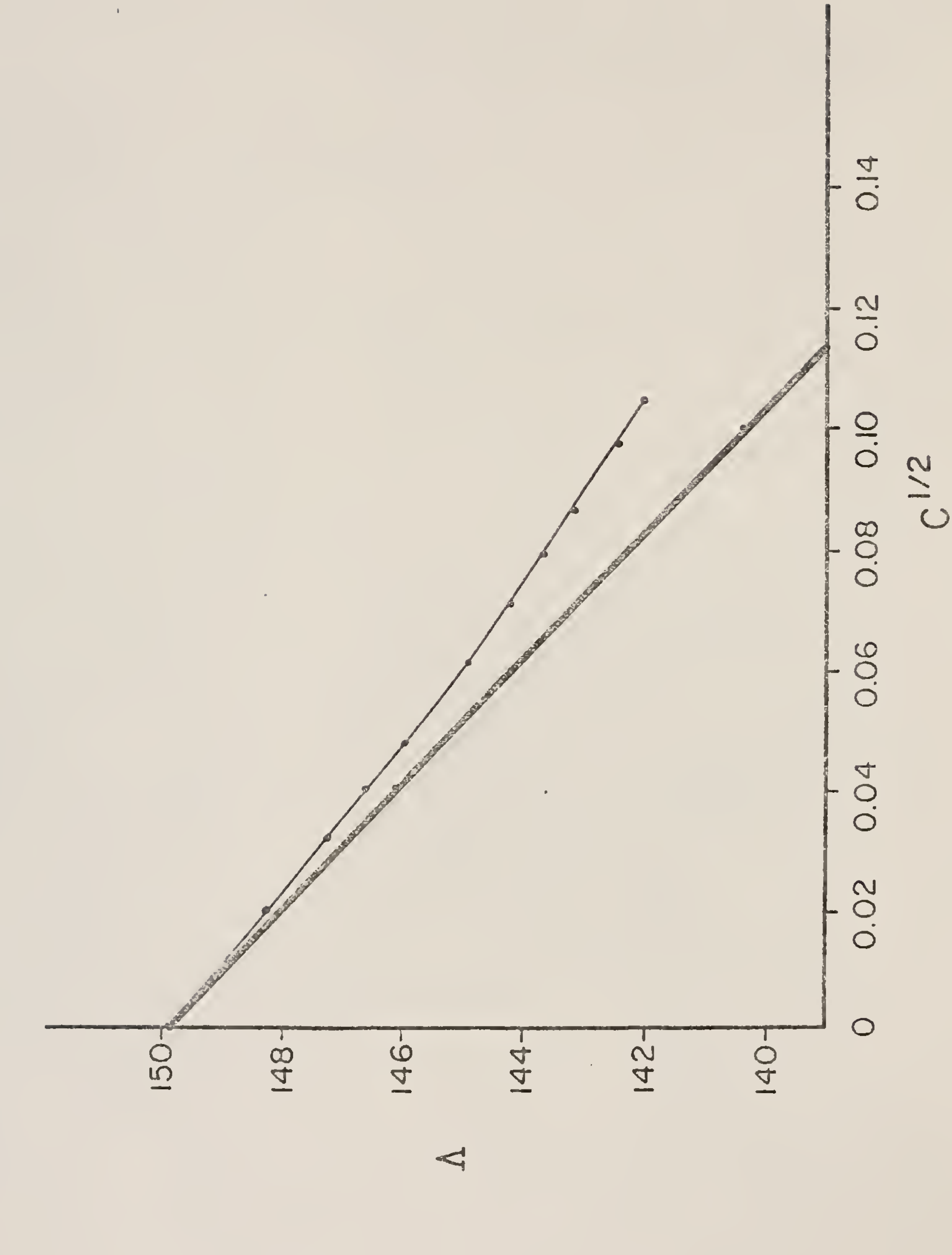
with the slope of the line being -S and the intercept being the limiting equivalent conductance, Λ^o. Experimentally, electrolytes that have negligible association give straight-line conductance plots which extrapolate quite closely to the actual Λ^o value. Such linear plots generally lie above the Debye-Hückel-Onsager slope.

In their book, "Electrolytic Conductance," Fuoss and Accascina[46] have described the behavior of the conductance curve as the association constant, K_a, is increased. As K_a increases from the negligible case described above, the conductance curve falls below the D-H-O slope and acquires an increasingly negative deviation as K_a increases. They have divided the curves into six types, making very careful mention of the fact that there is a continuous transition between the various types of curves. Data from this study to fit each type but one of the curves described by them were available and they are presented here.

Figure 18 is an example of the Type I conductance curve. It is for KCl in water at 25°C, and it is representative of

Figure 18

An example of Type I conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for KCl in water at 25°C. Bold line is the Debye-Hückel-Onsager slope.


Λ
150
148
146
144
142
140
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
$C^{1/2}$

the curves for strongly dissociated electrolytes. At very low concentrations, the curve lies on the D-H-O slope. As the concentration is increased, a positive deviation is noted, indicative of the dissociated electrolyte.

Figure 19 represents the Type II curve. Here, K_a is no longer negligible (characteristic of solvents with median values for the dielectric constant) and the curve lies slightly below the D-H-O slope. Extrapolation to zero concentration still yields a good value for Λ^o, however. The curve presented is for HCl in 25 M% sulfolane-water, at 30°C, and has an experimentally determined K_a of 2.37 mol^{-1} L. The curve is typical for electrolytes with association constants in this range, where ion association is just starting to take place.

Figure 20 represents a Type III curve, in this case for HCl in 50 M% sulfolane-water at 30°C. The experimentally determined K_a for this curve is 27.73 mol^{-1} L, and this Type III behavior will generally be seen with association constants ranging between 15 and 200 mol^{-1} L. Here extrapolation of the experimental curve will yield a value for Λ^o which is high compared to the actual value. It is at this point, where K_a has become sufficiently large to influence the extrapolation, that α, the degree of dissociation, should be incorporated into the theoretical treatment used to describe the behavior of the curve.

Figure 21 is an intermediate curve, representing the transition between Types III and IV. This curve is for HCl

Figure 19

An example of Type II conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for HCl in 25 M% sulfolane-water at 30°C. Bold line is the Debye-Hückel-Onsager slope.

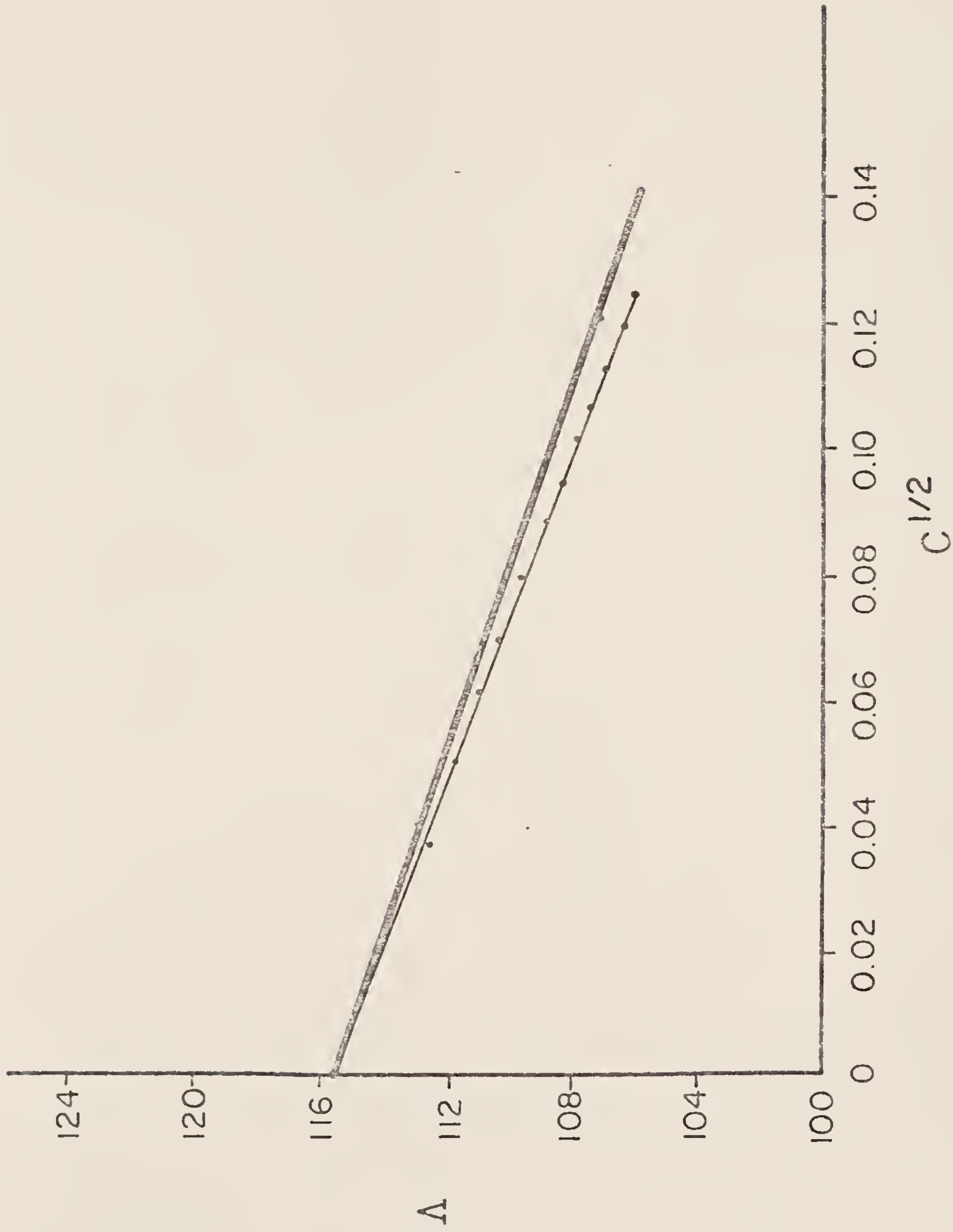

Λ
124
120
116
112
108
104
100
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
$C^{1/2}$

Figure 20

An example of Type III conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for HCl in 50 M% sulfolane-water at 30°C. Bold line is the Debye-Hückel-Onsager slope.

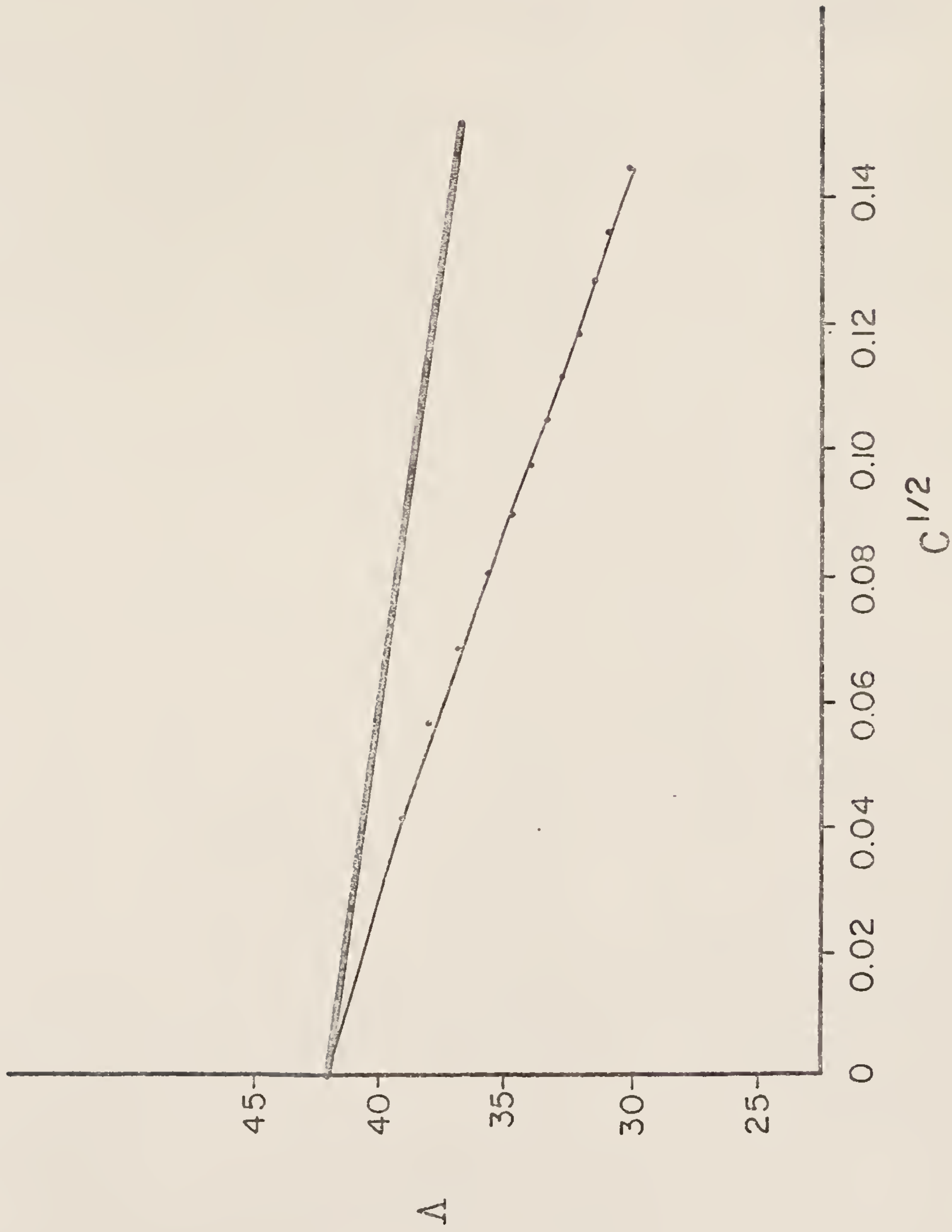
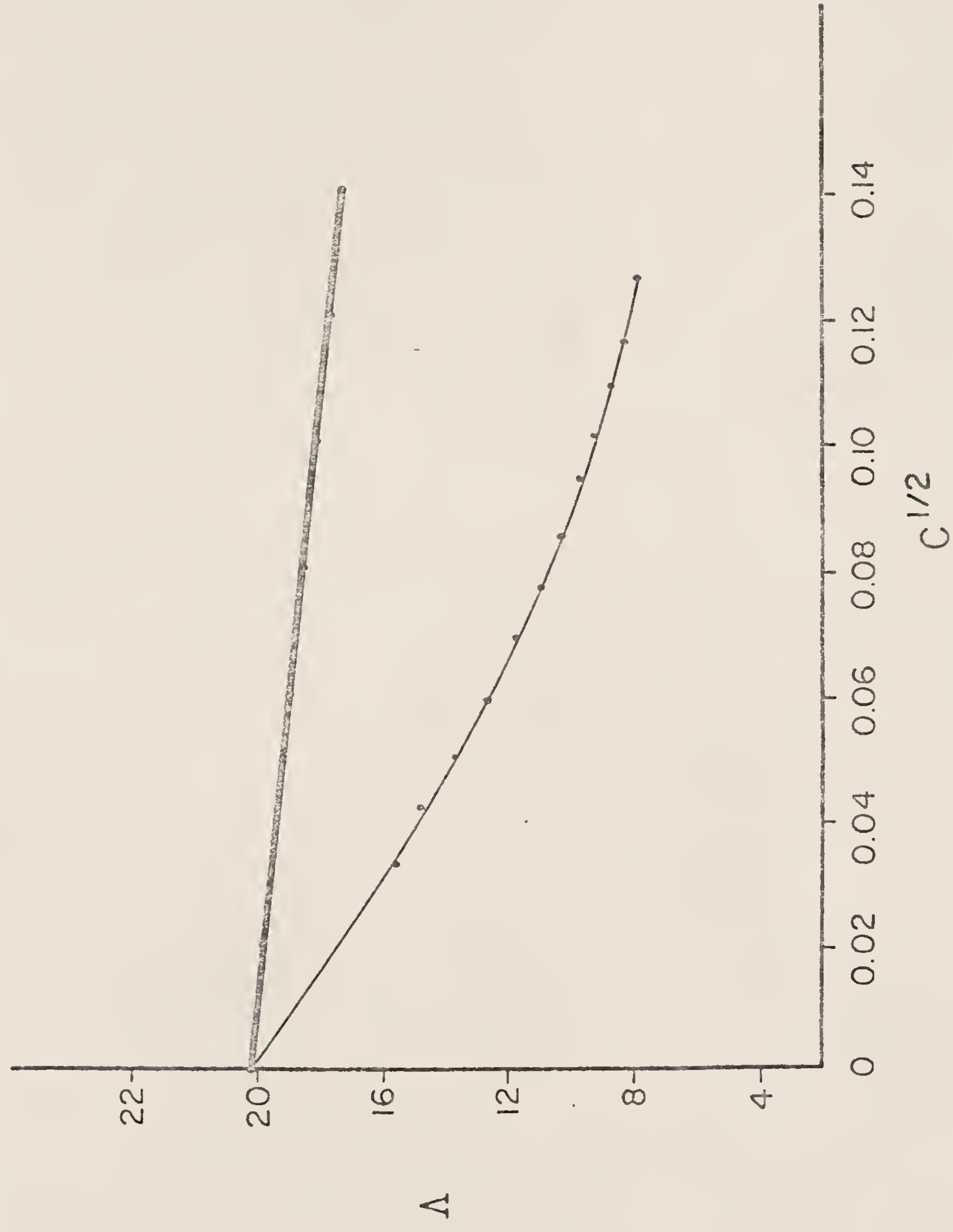

Λ
45
40
35
30
25
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
C^{1/2}

Figure 21

An example of conductimetric behavior intermediate to Types III and IV. A plot of equivalent conductance vs. the square root of the concentration for HCl in 75 M% sulfolane-water at 30°C. Bold line is the Debye-Hückel-Onsager slope.


Λ
22
20
16
12
8
4
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
$C^{1/2}$

in 75 M% sulfolane-water at 30°C, with K_a determined to be 288.13 mol^{-1} L. In this type of behavior, the inflection point in the curve has started to move into the low concentration region, and extrapolation of the curve to zero concentration will yield a value for Λ^o that is rather higher than the actual value.

Figure 22 is Type IV behavior, characterized by the inflection point of the curve being in the low concentration region. Extrapolation to zero concentration gives a value for the limiting conductance that is substantially in error. This curve is for HCl in 85 M% sulfolane-water at 40°C, with a K_a of 1336.2 mol^{-1} L.

For all of the curves described above, the full Pitts equation was found to yield excellent agreement between the calculated and the experimental values for the equivalent conductance. The expanded Pitts equation and the expanded Fuoss-Hsia equation were also found to yield satisfactory agreement. With the computer equipment available today, utilizing the proper program allows the use of a single theoretical treatment for conductance behavior, rather than the several treatments recommended by Fuoss and Accascina in their treatment of the conductance curves.

Figure 23 is representative of Type V behavior. This curve is for HCl in sulfolane at 40°C, and is characteristic of Type V behavior, showing very small values for Λ, and very high curvature in the low concentration region. Fuoss and Accascina state that there should also be a minimum

Figure 22

An example of Type IV conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for HCl in 85 M% sulfolane-water at 40°C. Bold line is the Debye-Hückel-Onsager slope.

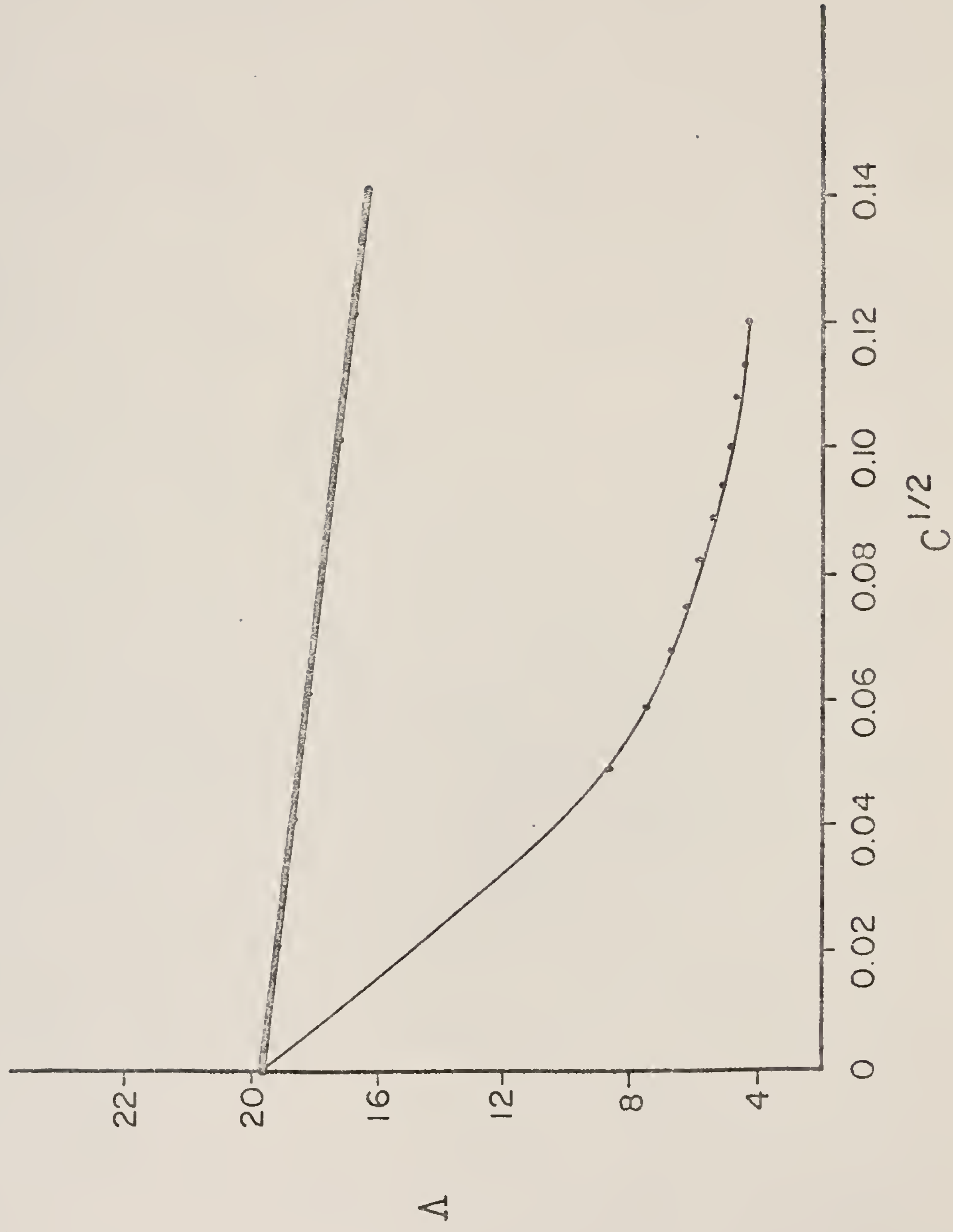
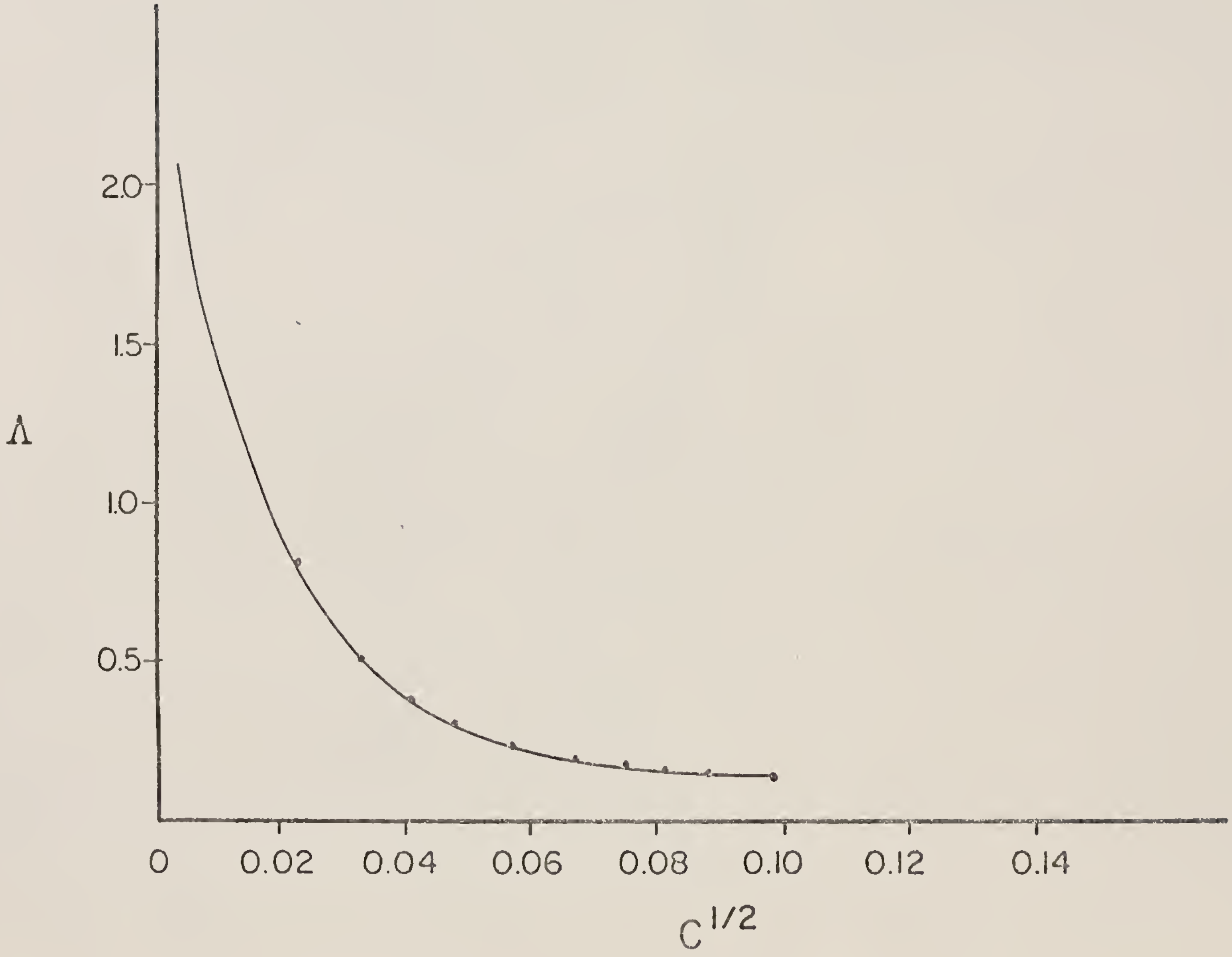

Λ
22
20
16
12
8
4
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
$C^{1/2}$

Figure 23

An example of Type V conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for HCl in 100 M% sulfolane at 40°C. The Debye-Hückel-Onsager slope is off-scale.


Λ
2.0
1.5
1.0
0.5
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
C^{1/2}

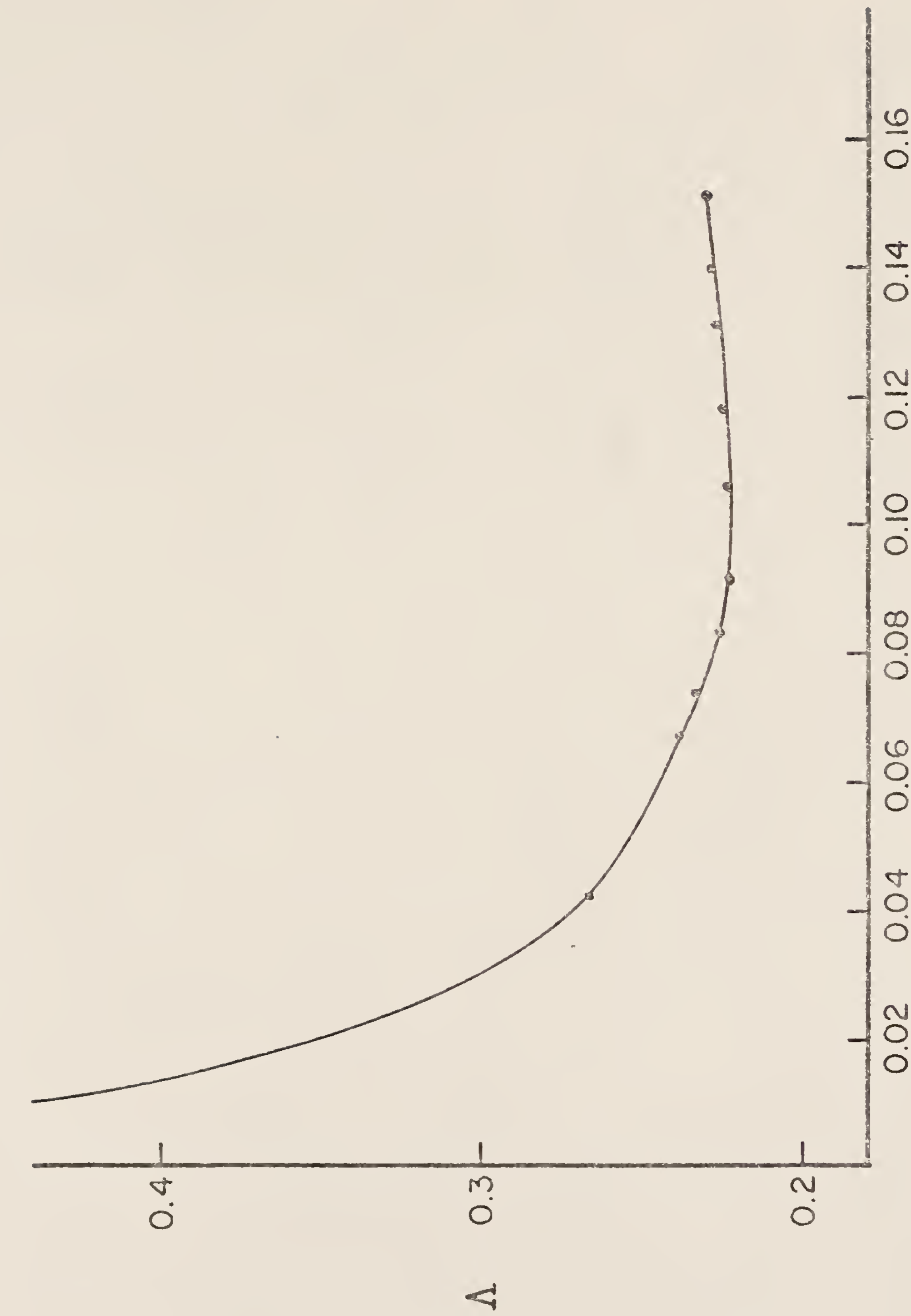
present, and attribute this behavior to a very high association constant coupled with triple ion formation. That is not noted here, however, and as will be discussed in a following section, triple ion formation in this case is unlikely.

Figure 24 is another example of Type V behavior, in this case for HCl in sulfolane at 30°C. Here, the minimum due to triple ion formation is noticeable; as the concentration increases, the concentration of triple ions increases, thus increasing the conductance. Neither the program for the full Pitts equation nor that for the expanded equations was capable of predicting this Type V behavior. Rather, a differing extrapolative method was utilized, that of Shedlovsky and Kay,[42] and will be discussed in a following section.

Type VI is associated with solvents of the hydrocarbon type, with very low dielectric constants, and is characterized by increasing conductance with concentration coupled with a complex curve form.

Figure 24

An example of Type V conductimetric behavior. A plot of the equivalent conductance vs. the square root of the concentration for HCl in 100 M% sulfolane at 30°C. The Debye-Hückel-Onsager slope is off-scale.


Λ
0.4
0.3
0.2
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
$C^{1/2}$

Ion Size Parameter

General

In the preceding chapters, mention has been made of the so-called ion size parameter. This is, in fact, a parameter introduced into the extended Debye-Hückel expression for the activity coefficient and into the main conductance equation via κa to account for the distance of closest approach of the ions in solution. There is a large element of arbitrariness in the choice of a value for this parameter, and in the course of this study several methods were employed to obtain a reasonable value.

A change in the value of a will cause a minor variation in the value of Λ^o, and a greater change in the value of K_a, produced by application of the conductance equations to the data. For electrolytes in high dielectric constant media, such as water, it has been noticed that as the ion size parameter is varied, the standard deviation between the calculated and experimental conductances, σ_Λ, goes through a minimum. This minimum in σ_Λ is taken as a criterion of best fit,[40,81] and the value of the ion size parameter at that point is used to generate the calculated conductance parameters.

This procedure was used in this study for Tris·HCl in water. A value of a was selected, and the conductance parameters were generated. The value of a was incremented, and the procedure was repeated. The value of a which yielded a minimum σ_Λ was the one selected for use in generating the results.

When dealing with solvents possessing medium to low dielectric constants, however, things become more complex. It has been noted that varying *a* will yield a minimum in σ_Λ, but it will be extremely shallow, or even a straight line.[82] In other cases, no minimum is observed; rather, there is a maximum! In such cases, the choice of *a* is rather arbitrary, with the value selected being "reasonable," whatever that means.

An example of this behavior of σ_Λ with respect to the value of *a* follows. For HCl in 75 M% sulfolane-water at 25°C, as shown in Table I, with an ion size of 5.99×10^{-8} cm, $\sigma_\Lambda = 0.121$. If this value for the ion size is changed to 3×10^{-8}cm, $\sigma_\Lambda = 0.125$. Very clearly, varying the value of the ion size parameter is not a suitable method for obtaining a reasonable value, in this case.

Because of the problem in choosing a reasonable value for the ion size parameter, several authors[40,83] have proposed using the Bjerrum critical distance as the ion size parameter. That is the procedure used, for the most part, in this study.

Bjerrum's distance

A fundamental question when dealing with conductance and ion association which must be answered is, what is an ion pair? At what point are ions considered paired, since at that point they will cease to contribute to conductance? Must they be in contact, or merely nearby? Most of the work which has been done with respect to a solution to this problem has been based on the early work of Bjerrum.[84]

It was Bjerrum who proposed that all oppositely charged ions within a certain critical distance be considered paired and no longer contributing to conductance. Basing his work upon a Boltzmann distribution function for electrostatic forces, Bjerrum obtained a probability function for finding an ion at a distance q from a central ion. A minimum was noted in this function, corresponding, for a 1:1 electrolyte, to:

$$q = \frac{z^2 e^2}{2\varepsilon kT} \qquad (55)$$

Ions closer together than this critical distance are, in the Bjerrum treatment, considered to be associated, since the probability of association increases very rapidly below this distance.

Applying the law of mass action to free and associated ions, Bjerrum derived an equation for the degree of association, $1 - \alpha$:

$$1 - \alpha = \frac{4\pi Nc}{1000} \int_{a}^{q} \exp\left(-\frac{z^2 e^2}{\varepsilon kTr}\right) r^2 dr \qquad (56)$$

From this, an expression can be derived for the association constant. This expression will be based totally on electrostatic considerations:

$$K_a = \frac{4\pi Na^3}{1000} \frac{e^b}{b} \qquad (57)$$

where:

$$b = \frac{2q}{a} \qquad (58)$$

Fuoss,[85] however, has stated that only those ions which are actually in contact with one another can be considered to be associated. His analysis of the problem yields the equation:

$$K_a = \frac{4\pi Na^3 e^b}{3000} \qquad (59)$$

It has been pointed out[86] that these electrostatic models, in all but the simplest cases, are totally inadequate for representing real-life behavior. Indeed, this was found to be the case in this study and will be further discussed when the results are examined. In any case, quoted results for Λ^o and K_a should always make mention of the ion size value used in the calculations, and that rule is adhered to in this study.

Choice of Conductance Equation

After all the data are gathered, and after a method of arriving at a reasonable value for the ion size parameter is decided upon, there still remains the choice of which conductance equation to use. Each has advantages and disadvantages. The expanded equations, both Pitts and Fuoss-Hsia, take very little time on the computer. However, they do tend to break down at high values of κa. The full Pitts equation is generally applicable to conductance data but takes a rather long time before the results are computed. Of course, where the expanded equations work, they could be employed, and where they do not, the full Pitts equation program could be utilized.

Perhaps the best method of deciding which equation to use is to examine how well the equation can fit the data; that is, which equation can theoretically synthesize equivalent conductance values closest to those experimentally obtained. In this way, the logical choice of equation would be that which gives the best fit.

Table VII presents the results for HCl in sulfolane-water solvents, calculated by all three equations. Examination of the values of σ_Λ reveals that, in general, the full Pitts equation gives a more satisfactory fit to the conductance data than either of the expanded equations. This, coupled to the fact that the expanded equations broke down for several of the solvent systems studied, is the

TABLE VII

Comparison of conductance parameters generated by full Pitts (PITTSEQN) and expanded equations (EXPEQNS) programs.

Solvent	Full Pitts			Expanded Pitts			Expanded Fuoss-Hsia		
	Λ^o	K_a	σ_Λ	Λ^o	K_a	σ_Λ	Λ^o	K_a	σ_Λ
25 M%, 25°C	104.295	2.54	0.056	104.292	2.46	0.053	104.308	2.20	0.058
25 M%, 30°C	115.495	2.37	0.097	115.404	2.03	0.077	115.582	2.25	0.116
25 M%, 40°C	136.504	4.64	0.114	136.219	4.06	0.128	136.674	4.60	0.130
50 M%, 25°C	36.344	20.30	0.022	36.316	19.78	0.018	36.367	19.96	0.023
50 M%, 30°C	42.108	27.73	0.053	41.969	26.25	0.056	42.145	27.48	0.057
50 M%, 40°C	49.597	26.26	0.039	49.575	25.88	0.040	49.614	25.78	0.039
75 M%, 25°C	18.929	303.19	0.121	18.791	293.84	0.121	18.880	298.23	0.123
75 M%, 30°C	20.194	288.13	0.154	20.130	283.48	0.154	20.165	284.54	0.157
75 M%, 40°C	26.806	319.47	0.093	26.799	318.58	0.093	26.799	317.31	0.093
85 M%, 25°C	12.374	756.14	0.039	12.139	714.17	0.046	12.225	726.32	0.043
85 M%, 30°C	12.350	526.52	0.172	11.909	471.14	0.199	12.154	498.79	0.188
85 M%, 40°C	19.698	1336.2	0.058	19.503	1299.5	0.062	19.502	1296.0	0.061

Sulfolane-water solvent system, HCl as solute.

Bjerrum's distance used as the ion size parameter.

rationale by which the full Pitts equation was chosen for the analysis of data in this study. All results presented, with the exception of those labeled otherwise, such as in Table VII, are generated with the full Pitts equation, using the Bjerrum critical distance as the ion size parameter.

2-Methoxyethanol - Water Solvent System

General

The results for this study were presented in Table III. Those results utilize the Bjerrum critical distance, which in the solvent studied, 80 W% MetOH-H_2O, is 8.7×10^{-8} cm. Analysis of the data by varying the ion size parameter showed a minimum in the plot of σ_Λ vs. a. As an example of how the varying value of the ion size parameter affects the results, the conductance parameters generated by this method are listed below.

TABLE VIII

Calculated conductance parameters for the 80 W% MetOH-H_2O solvent system, utilizing the variation in a value method.

Solute	Λ^o ($S\ cm^2\ mol^{-1}$)	K ($mol^{-1}\ L$)	a ($cm \times 10^{-8}$)	σ_Λ
HCl	53.066	7.85	4.0	0.025
NaCl	31.651	10.28	4.5	0.011

Sodium acetate was found to give a maximum in σ_Λ rather than a minimum.

Variation of the ion size parameter from the Bjerrum distance of 8.7×10^{-8} cm to about half that value has caused a change of only about 0.5% in Λ^o; at the same time, the values for K_a have changed by almost 100%. The Bjerrum distance is used throughout this study, and the results are those found in Table III.

The value for the association constant of HCl, 14.81 mol^{-1} L, corresponds to a pK_d of 1.17. This is in good agreement with the results of Merken et al.,[17,18] who report a pK_d of 1.20. Analysis of their conductance data with the full Pitts equation yielded value for pK_d of 1.22, still in excellent agreement.

It is of interest to note that, in a previous paper, Thun and his coworkers[16] estimated K_a for HCl from EMF measurements. Their value of 4.902 mol^{-1} L is somewhat lower than that found conductimetrically, pointing out the value of direct measurement over roundabout estimates.

It is possible, using the Bjerrum and Fuoss theories of association, to obtain a value for K_a based solely on electrostatics. For the 80 W% MetOH-H_2O system, using the Bjerrum distance, this is 18.40 mol^{-1} L with the Bjerrum theory and 12.27 mol^{-1} L with the Fuoss theory. It can be seen that there is fair agreement with the experimental result, indicating that electrostatic effects go a long way toward accounting for the association of HCl in the system.

It has been postulated[17] that in this system the proton is highly solvated by water. If that is the case, the proton and the Cl^- ion would be held further apart, and may explain why the association constant for HCl is less than for NaCl.

The value for K_a of HAc of 1.24 x 10^8 mol^{-1} L was not derived by the full Pitts equation. This electrolyte showed Type V behavior, as explained in a preceding section, and the Pitts equation was unable to account for this behavior.

Use was made here of the extrapolative method devised by Shedlovsky and Kay[42] for the treatment of their data for HAc in methanol-water solvents, and it is applicable to systems where the conductance due to the solvent is an appreciable fraction of the total conductance.

Shedlovsky-Kay Extrapolation

This extrapolative method for the determination of K_a for very weak acids is quite useful, provided one major condition can be fulfilled. For application of this method it is necessary to have an estimate of Λ^o. The usual method of obtaining this is to use the Kohlrausch law of independent migration. According to this, the moving ions do not influence each other and, consequently, the limiting conductance of the ions remains constant despite the other ions in solution. Thus Λ^o can be determined by combining measurements on other electrolytes. For 80 W% MetOH-H_2O, the value of Λ^o for HAc was synthesized from the values for HCl, NaCl, and NaAc, as follows.

The limiting conductance of HAc is made up of the contributions of the ionic conductances:

$$\Lambda^o_{HAc} = \lambda^o_H + \lambda^o_{Ac} \tag{60}$$

We can obtain this combination of ionic conductances by the combination of Λ^o values for the aforementioned electrolytes:

$$\Lambda^o_{HAc} = \Lambda^o_{HCl} + \Lambda^o_{NaAc} - \Lambda^o_{NaCl} = \lambda^o_H + \lambda^o_{Cl} + \lambda^o_{Na} + \lambda^o_{Ac} - \lambda^o_{Na} - \lambda^o_{Cl} = \lambda^o_H + \lambda^o_{Ac} \tag{61}$$

For this solvent system, the procedure yields a value of Λ^o for HAc of 47.064 S cm^2 mol^{-1}. Using this value, the Shedlovsky-Kay extrapolation can be applied.

In this extrapolation, the equivalent conductance which contains the solvent correction is not used, but rather one thousand times the specific conductance. This quantity, abbreviated L, is plotted vs. a function of the square root of the concentration. It is during this extrapolation, in calculating the value of the function of $c^{\frac{1}{2}}$, that the solvent correction is applied. With L_o as one thousand times the specific conductance of the solvent, the Shedlovsky-Kay extrapolation equation becomes:

$$L = \frac{\Lambda^o K_a^{\frac{1}{2}} c^{\frac{1}{2}}}{Sf}\left(1 - \frac{\Lambda^* S}{\Lambda^o}\left(1 - \frac{L_o}{L}\right)\right)^{\frac{1}{2}} - L_o \qquad (62)$$

where f is the activity coefficient, Λ^* is L divided by the concentration, and S is a function of c and Λ^o.

The computer program, "SHEDKAY," was designed to follow the recommendations of the authors of the paper as to the proper extrapolation technique. Using that program, a value was obtained for K_a of 1.24 x 10^8 mol^{-1} L, or a pK_d of 8.09. This may be compared to values of 6.71 in 80 W% methanol-water[42] and 6.98 in 80 W% ethanol-water.[87,88] It can be seen that in all three alcohols acetic acid exists in an essentially ion-paired form, and in all three it is far more associated than in water (pK_d = 4.76). This is in keeping with the idea that water can solvate the proton more easily than can the bulky alcohols. The Λ^o value in 80 W%

$MetOH-H_2O$ is much higher than would be expected with an essentially associated eletrolyte, and may be attributed to the limited proton jump mechanism in the alcohols.[17,18] A preliminary value for pK_d of HAc in 80 W% $MetOH-H_2O$, determined via EMF studies in this laboratory[71] is 7.39, a considerable difference from that determined by this study. The reason for the difference remains unexplained.

At 25°C, the K_a for Tris·HCl in water was found to be 1.01 mol^{-1} L, and in 80 W% $MetOH-H_2O$ to be 29.46 mol^{-1} L. These results may reflect the lesser ability of the alcohol to solvate the $TrisH^+$ ion which, with three OH groups, can enter into hydrogen bonding with the water structure. This interaction with the water structure is seen in the low limiting ionic conductance found for the $TrisH^+$ ion in water.[72] It is interesting to note that, in water at 25°C, using the ion size determined for Tris·HCl, the Bjerrum association constant is 0.78 mol^{-1} L and the Fuoss association constant is 0.70 mol^{-1} L. Both are reasonably close to the experimentally determined K_a of 1.01 mol^{-1} L, indicating that the association is primarily electrostatic in nature. This is not the case in 80 W% $MetOH-H_2O$, where Bjerrum and Fuoss K_a values are, respectively, 18.4 and 12.3 mol^{-1} L. The experimentally determined constant of 29.46 mol^{-1} L indicates that electrostatics cannot wholly explain the association found. More will be said about this later.

Sulfolane-Water Solvent System

General

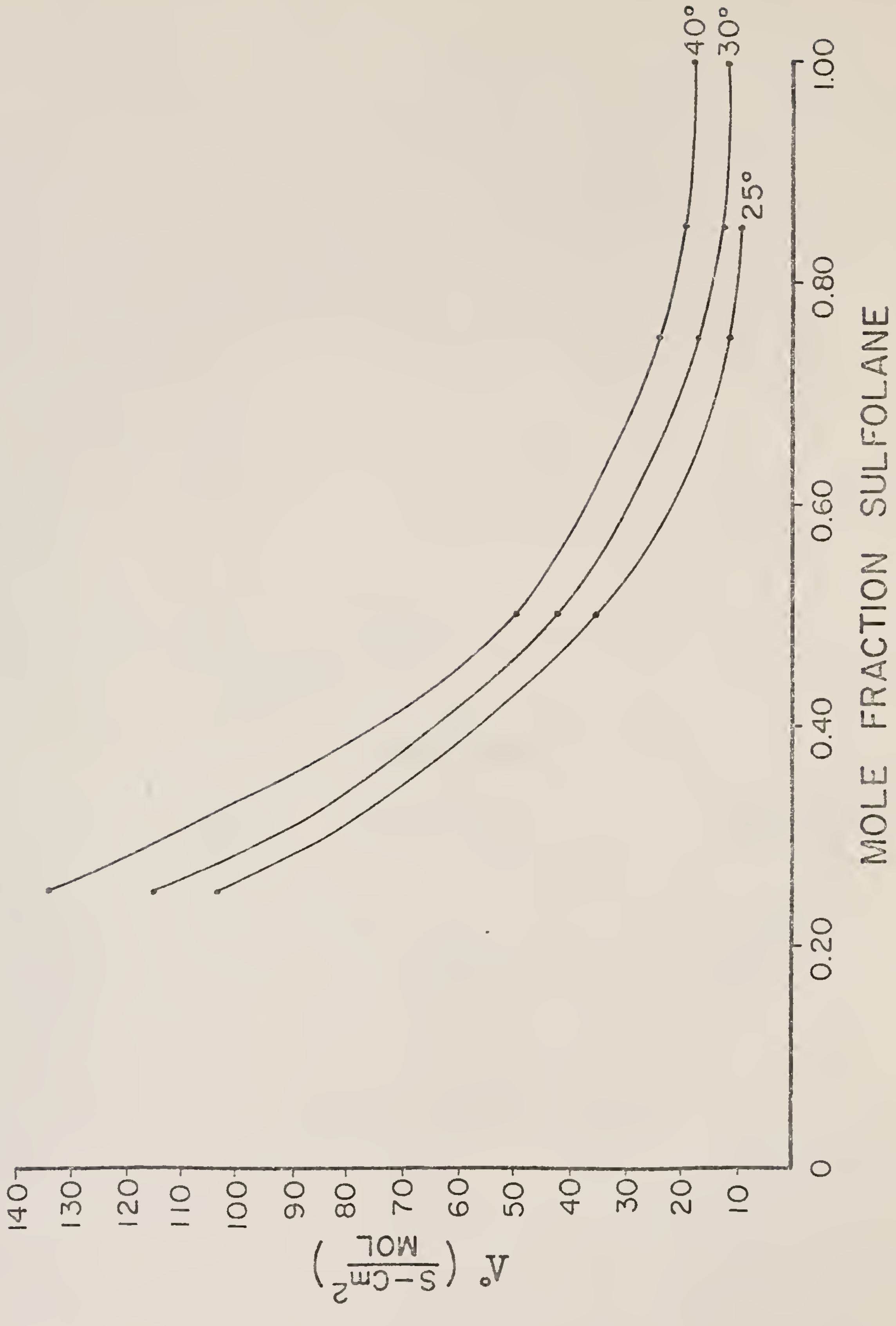
Sulfolane is probably the perfect example of a dipolar aprotic solvent. A number of conductimetric studies have been done using sulfolane as the solvent, almost universally at 30°C.[9,89-99] Very little work has been done with sulfolane-water mixed solvents.[95-98,100,101] With this in mind, a study of the conductance of HCl in sulfolane and sulfolane-water solvents at several temperatures was undertaken.

The conductance results for this aspect of the study are summarized in Table I. Those calculations were made with the Bjerrum critical distance as the value for the ion size parameter in both the Pitts equation and the expression for the activity coefficient. The results for pure water were obtained by applying the full Pitts equation to the data of Owen and Sweeton[68] and Stokes.[69,70] HCl in pure sulfolane exhibited Type V conductimetric behavior and is discussed separately.

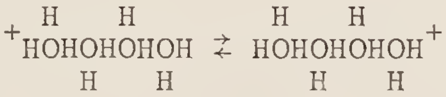
Figure 25 shows the behavior of the limiting equivalent conductance with respect to the mole fraction of sulfolane in the solvent. As can be seen, the addition of small amounts of sulfolane to water cause a dramatic decrease in the limiting conductance of HCl. This may be attributed to the disruption, by sulfolane, of the water structure, and a consequent dramatic decrease in the probability of the proton jump mechanism taking place.

Figure 25

A plot of the limiting equivalent conductance of HCl vs. the mole fraction of sulfolane in the solvent at various temperatures. The limiting equivalent conductance in water (0 mole fraction sulfolane) is off-scale.


Λ° (S-cm²/MOL)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.20
0.40
0.60
0.80
1.00
MOLE FRACTION SULFOLANE
40°
30°
25°

It is the proton jump mechanism that is responsible for the anomalously high conductances of the proton and the hydroxide ion in water. This is due to the fact that these ions are actually fragments of the solvent, water. With the hydrogen-bonded structure of water, there is no need for the ions to move. Rather, the proton (or hydroxide ion) is transferred from a hydronium ion to a water molecule, which transfers it on, etc. The result is no great movement of the ion per se, but a very rapid movement of the charge along the chain of hydrogen-bonded water molecules. The proton jump mechanism is diagrammed in Figure 26.



$$^{+}\mathrm{H}\overset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\underset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\overset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\underset{\mathrm{H}}{\mathrm{O}}\mathrm{H} \rightleftarrows \mathrm{H}\overset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\underset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\overset{\mathrm{H}}{\mathrm{O}}\mathrm{H}\underset{\mathrm{H}}{\mathrm{O}}\mathrm{H}^{+}$$

Figure 26

The proton jump mechanism.

If the water structure were disrupted, the length of the structural chains would decrease, and a decrease in the conductance of the proton would be expected. This is exactly what is noted when sulfolane is added to water, and ties in well with the structural considerations noted earlier. By the time the solvent contains 25 M% sulfolane, the limiting conductance has decreased by 75%, indicating that the proton jump mechanism (and hence the water structure) has been, for the most part, disrupted.

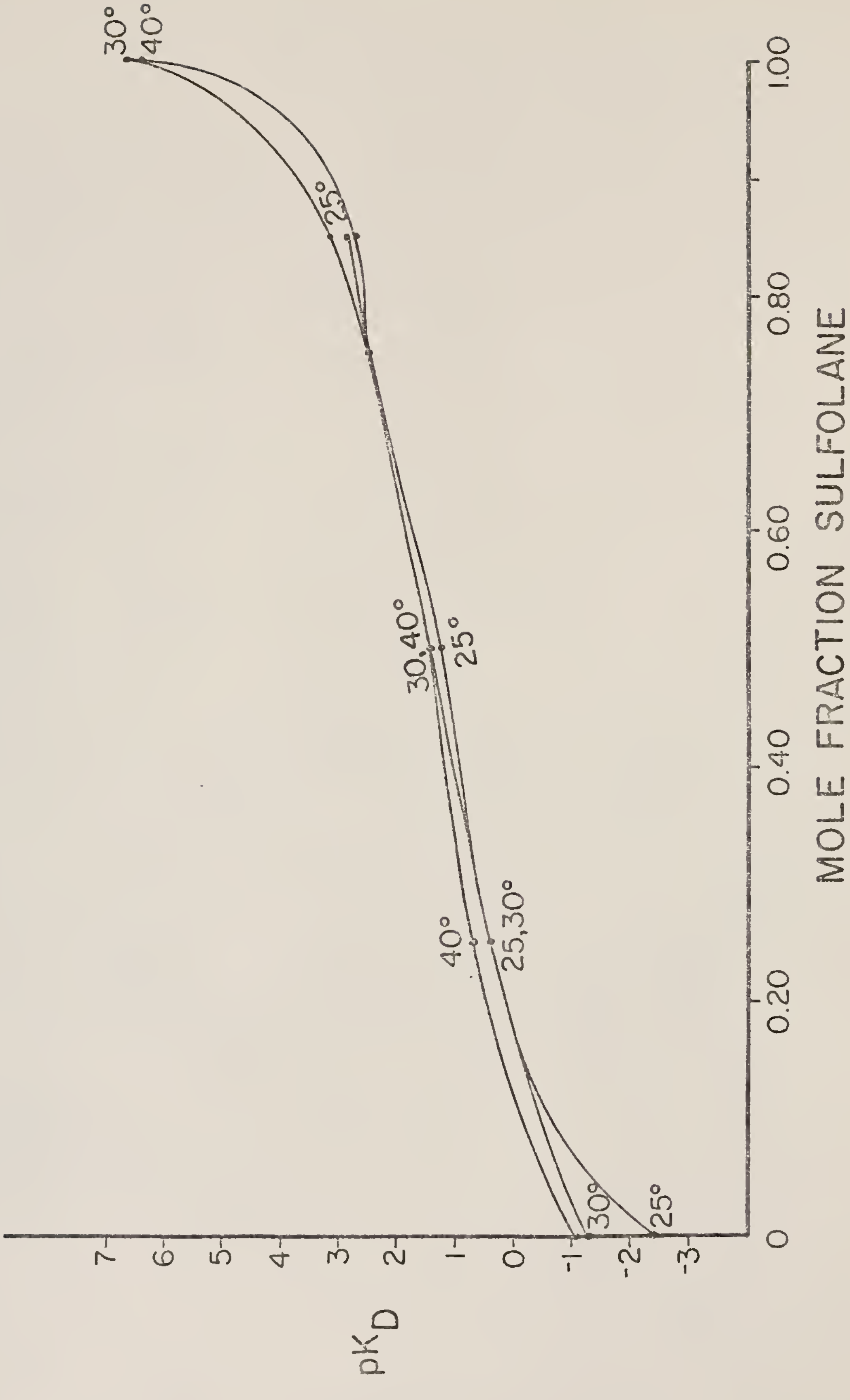
Figure 27 is a plot of the pK_d (= log K_a) of HCl vs. the mole fraction of sulfolane. As can be seen, there is almost a linear dependence of pK_d on mole fraction of sulfolane for most of the solvent mixtures, the exceptions being at either end of the plot. From approximately 10 M% to 90 M%, there is a linear dependence on mole fraction of sulfolane. Since the amount of ionization is directly proportional to the strength of solvation of the ions involved, it is quite apparent that as the amount of sulfolane in the solvent increases, the solvation of the ions, in particular the proton, decreases.

The rather precipitous drop in pK_d as small amounts of water are added to sulfolane probably corresponds to the hydration of the proton to form hydronium ions, thus promoting dissociation. Milanova et al [102] have pointed out that as water is added to acid solutions in sulfolane, the species $H(H_2O)_n^+$ are formed, with the primary species being $H(H_2O)_4^+$. Once this species is formed, the increase in dissociation is far more moderate, probably indicative of longer chains of water molecules forming as the water content is increased.

Bates and Pawlak[103] have pointed out the linear dependence of pK_d on the mole fraction of sulfolane in the range X_s = 0 to 0.8 for a variety of weak acids, similar to the dependence found here for HCl. As they assumed, the pK_d does rise significantly (to say the least) between mole fractions of 0.8 and 1.0.

Figure 27

A plot of the pK_d (= log K_a) of HCl vs. the mole fraction of sulfolane in the solvent at various temperatures.


pK$_D$
7
6
5
4
3
2
1
0
-1
-2
-3
0
0.20
0.40
0.60
0.80
1.00
MOLE FRACTION SULFOLANE
30°
40°
25°
30,40°
25°
40°
25,30°
30°
25°

Petrella and his co-workers[96,97] have examined the conductance of HCl in sulfolane-water mixtures at 35°C, which would complement the 25, 30, and 40°C measurements of this study. Unfortunately, they avoided systems where association was not negligible and, as a result, intercomparison of results is not feasible. Their limiting conductance values, plotted in the manner of Figure 25, fall roughly between the curves for 30 and 40°C, as expected. However, their values for K_a appear to be rather high compared to the results obtained in this study. For $X_S = 0.3116$, they report a K_a of 51 mol^{-1} L, whereas interpolating with Figure 27 yields a value of approximately 7.25 mol^{-1} L. Again, at $X_S = 0.1583$, they report $K_a = 26$ mol^{-1} L, and using Figure 27 a value of less than 1 mol^{-1} L is obtained. The reasons for this difference may lie in the manner of treating the raw conductance data, since they did not use a solvent correction when calculating the equivalent conductances, and they treated their data with the Fuoss-Onsager equation for obtaining results.

The variation of K_a with temperature for the sulfolane-rich solvents is worthy of mention. The value of K_a goes down with increasing temperature from 25 to 30°C, but then increases from 30 to 40°C. A possible rationale for this behavior follows. As the temperature increases, the dielectric constant of the solvent decreases, and this will promote the formation of ion pairs. At the same time, increasing temperature increases the Brownian motion within the system, which would tend to break up ion pairs. The two competing effects may be responsible for this strange behavior.

For these systems, the electrostatic association models clearly show inadequacies. At 25 M% sulfolane-water, at 25°C, the K_a from the Bjerrum theory is 2.88 mol^{-1} L; from the Fuoss theory it is 1.92 mol^{-1} L. The experimentally determined value of 2.54 mol^{-1} L is in rather close agreement. Interestingly enough, the method of variation of the ion size parameter mentioned earlier worked well for this system. Clearly, the system may, for the most part, have its behavior explained in terms of electrostatics.

For the rest of the sulfolane-water solvents, however, this is not the case. For 50-, 75-, and 85-M% sulfolane-water solvents at 25°C, the Bjerrum theory predicts values for the association constants of 4.30, 6.01, and 6.63 mol^{-1} L respectively; for the Fuoss theory, 2.87, 4.01, and 4.42 mol^{-1} L, respectively. Comparison with the actual experimental values shows, quite clearly, that electrostatics can no longer explain the ion association. It now becomes more a matter of solute-solvent interactions, as previously pointed out.

The major anomaly on the plot of pK_d vs. mole fraction sulfolane (Figure 27) is quite clearly at 1.0 mole fraction sulfolane. Such a drastic change in pK_d is evidence of a fundamental change within the solution, and that is explored next.

Pure Sulfolane

Since the first conductance study in sulfolane, by Burwell and Langford in 1959,[89] there have been a number of studies of the solvent, but many questions yet remain about solution processes in this most interesting solvent.

Most studies in the past have been done at 30°C, since this is the first even temperature above the melting point of sulfolane. Such studies have shown that the ability of sulfolane to solvate ions is in direct proportion to the size of the ion. Electrolytes containing large ions, such as tetraphenylarsonium, appear to be largely dissociated in sulfolane solutions,[9,89,91,92,98,99] indicating that they are solvated well by the solvent. By contrast, electrolytes with small ions, such as the alkali halides, have been found to exist primarily in undissociated forms.[9]

There have been attempts to set up acidity and basicity scales in sulfolane, with limited success.[104-109] Examining freezing-point depressions caused by sulfuric acid, Arnett[105] came to the conclusion that sulfolane will not protonate. Whiting and his coworkers,[108] in the course of setting up such a scale, came to the conclusion that acids with large anions (e.g., ClO_4^-, PF_6^-) were dissociating simply, while the mineral acids were subject to homoconjugation as well:

$$HCl \rightleftarrows H^+ + Cl^- \tag{63a}$$

$$HCl + Cl^- \rightleftarrows HCl_2^- \tag{63b}$$

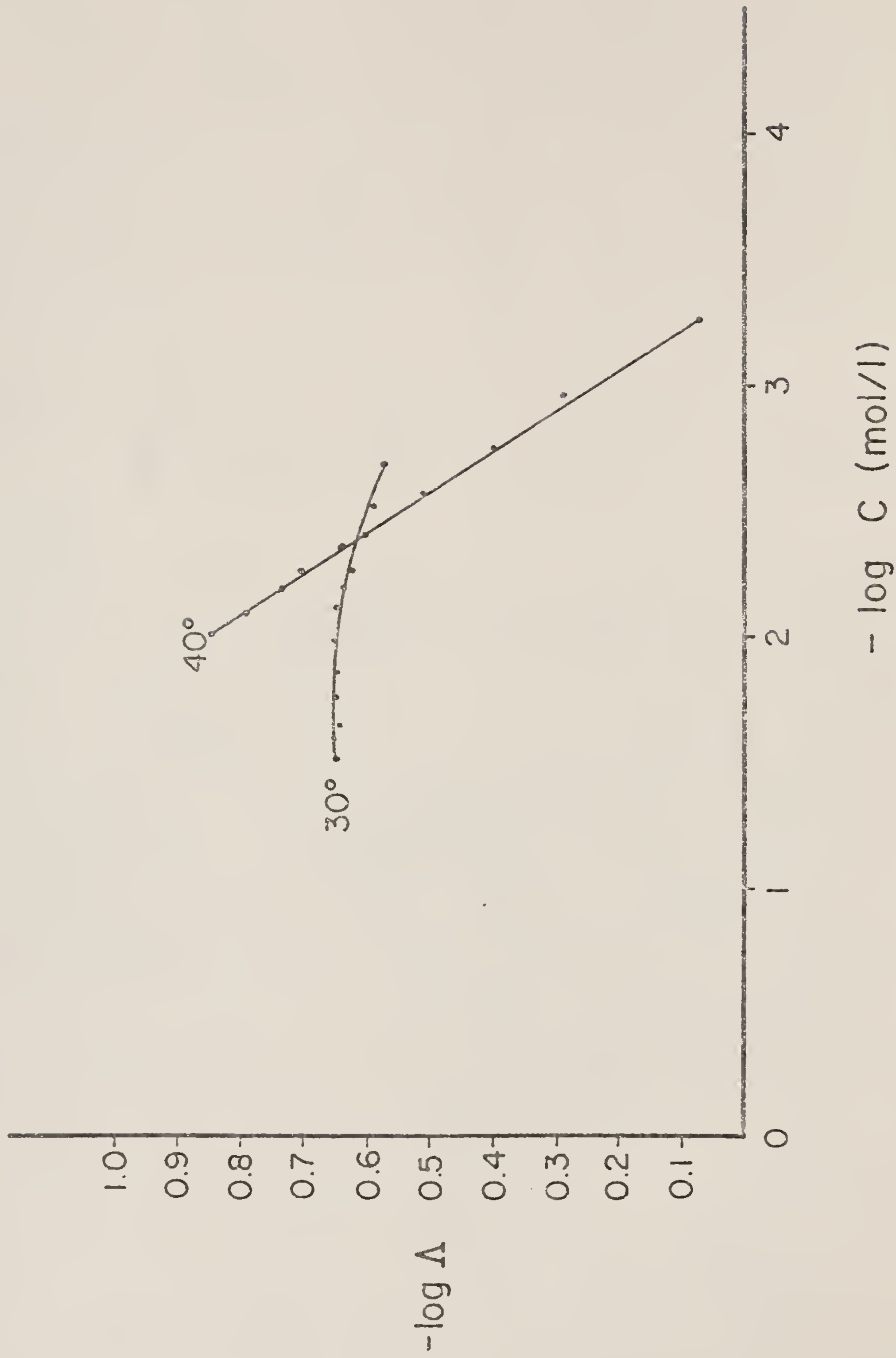
Coetzee[106,107] has used sulfolane as a medium for conductimetric titrations and obtained a pK_d for HCl by titration with silver perchlorate potentiometrically. He obtained a value of 14.5. Petrella and coworkers[96,97] determined K_a for HCl conductimetrically at 35°C and obtained a value of pK_d of 9.0. There is, evidently, some confusion about the properties of sulfolane as a solvent.

The conductance of sulfolane, at 30°C, varies very little with concentration, remaining at about 0.22 S cm^2 mol^{-1}. This is a perfect example of Type V conductance, and none of the theoretical equations was able to account for this type of behavior. A different approach was tried, that suggested by Caruso and his coworkers.[110]

The method of Caruso involves plotting $-\log \Lambda$ vs. $-\log c$. The intercept of the plot provides information about K_a, and the slope of the line varies with the nature of the dissociation process. Figure 28 shows such Caruso plots for HCl in sulfolane at 30°C and 40°C. The plot of 40°C has a slope of approximately -0.5, indicating a simple dissociation process (Equation 63a). The intercept for such an ionization process has the magnitude $-\frac{1}{2}\log K_d\Lambda^{o2}$. The limiting conductance cannot be obtained by extrapolation and is obtained from literature values. Della Monica and coworkers[90] report the value of λ^o_{Cl} as 9.30, and $\lambda^o_{ClO_4}$ as 6.68 S cm^2 mol^{-1}. Coetzee[106] gives the limiting conductance of $HClO_4$ as 15. Combining this information gives $\lambda^o_H = 8.3$ and Λ^o for HCl = 17.6 S cm^2 mol^{-1}. This yields a value of K_a of 6.14×10^{-6} mol^{-1} L, or a pK_d of 6.79.

Figure 28

A plot of -log (equivalent conductance) vs. -log (concentration) for HCl in sulfolane at 30°C and 40°C, after the method of Sellers et al.[110] The slope of the 30°C plot is approximately zero; the slope of the 40°C plot is approximately -0.5.


-log Λ
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
- log C (mol/l)
40°
30°

Since the process is a simple dissociation, the Shedlovsky-Kay extrapolation for weak acids was applied. This gave a value of 2.45×10^6 mol^{-1} L for K_a, or pK_d = 6.39. Since this method of arriving at K_a involves fewer approximations, these are regarded as the best values in this study.

Examination of Figure 28 shows that, at 30°C, the plot of $-\log \Lambda$ vs. $-\log c$ has a slope of zero. Caruso has indicated that this is typical of a simple dissociation coupled with homoconjugation (Equations 63 a & b). This is in accord with the results of Whiting, mentioned earlier.

Benoit and his coworkers have studied the system HCl in sulfolane at 30°C.[111-112] Utilizing calorimetry and proton NMR, they concluded that, in sulfolane, HCl_2^- forms, and that the formation constant is approximately 350. Their finding is in accord with the Caruso plot at 30°C. For this process, Caruso gives the magnitude of the intercept as $-\frac{1}{2}\log 4K_1K_2\ \Lambda^{o2}$, with K_2 the formation constant of the homoconjugate. Utilizing Petrella's estimate[96] of the limiting conductance for the ion pair (IP) $H^+\ HCl_2^-$, of 13, K_a is calculated to be 4.72×10^6 mol^{-1} L, or a pK_d of 6.67. The Shedlovsky-Kay extrapolation here gave a value of 5.23, rather different from that arrived at from the Caruso plot--unlike the situation at 40°C, where the two methods gave fair agreement. This may be due to the difference in dissociation process.

For HCl in pure sulfolane, too many approximations are involved to leave the values of K_a with much certainty except the order of magnitude. The results here indicate a pK_d on the order of 6.5. This is in very sharp disagreement with that estimated by Coetzee,[107] $pK_d = 14.5$. One must seriously question several of the assumptions made by Coetzee in arriving at that conclusion, not the least of which are the assumption of an activity for the protonated sulfolane and assuming that HCl_2^- has no effect whatever.

Petrella and his coworkers[96,97] report findings for HCl in sulfolane at 35°C similar to those found in this study at 30°C. They determined a pK_d, by the same method, of 9. As previously pointed out, the K_a results of that study are consistently higher than those found here, and this is no exception. Recalculating Petrella's results, however, using the values they specify, gives a pK_d of 8.4, more reasonable in light of the value determined in this study, 6.67, although the discrepancy is still perplexing.

The explanation for such high association must lie in the solvation, or lack thereof, of the ions. Parker[113,114] has shown that in dipolar aprotic solvents such as sulfolane, the solvation of anions will be, for the most part, a result of ion-dipole interactions coupled with interactions caused by the mutual polarizability of the anion and the solvent molecule. Thus the observation that electrolytes with large anions are more solvated makes more sense. By the same token, small anions such as chloride will be less solvated; indeed, in sulfolane, chloride exists as a naked, and hence highly reactive, ion.

The proton basicity of sulfolane has been shown to be very low, on the order of -12.9 for pK_{SH^+}, making it one of the most protophobic solvents.[115] Given this small tendency to solvate the proton, coupled with highly reactive "naked" chloride ions and sulfolane's ability to solvate large anions, the formation of the homoconjugate complex HCl_2^- is not surprising. Indeed, it has been shown that this species forms in a number of dipolar aprotic solvents,[113,116] the most notable being acetonitrile.[4,117-119] The naked chloride ion in sulfolane has been found to be sufficiently reactive to form the homoconjugate $AgCl_2^-$.[120]

What is, perhaps, most surprising is that at 40°C, the conductance data fail to reveal any evidence of homoconjugation. The Caruso plot shows a line with a slope of about -0.5, indicating simple dissociation, and the dissociation constant determined via that method agrees well with that determined by the Shedlovsky-Kay extrapolation. With almost all studies of sulfolane done at 30°C, it is most difficult to interpret this fact.

As Parker has pointed out,[113] sulfolane is a highly associated liquid at 30°C, retaining much of the structure it had as a solid. This is evidenced by the high viscosity. The sharp drop in the viscosity when the temperature is raised to 40°C is indicative of a decrease in the structuring of the solvent. This probably plays a role in the change of ionization process which occurs perhaps by facilitating the solvation of the anion. This being the case, it is conceivable that the behavior of sulfolane as a solvent at 30°C is not typical of the behavior of true liquid sulfolane.

NM_2Py-Water Solvent System

Far less work has been done using 1-methyl-2-pyrrolidinone (NM_2Py) as a solvent than has been done with the sulfolane solvent systems,[13,77,79,121-126] and there are few conductance studies.[125,126] Since both sulfolane and NM_2Py have similar physical characteristics, it was thought that a study of the conductimetric behavior of HCl in NM_2Py and NM_2Py-water solvents would be useful for comparative purposes, and might help shed additional light on the properties of this useful solvent.

The conductance results for this portion of the study appear in Table II. They were calculated using the Bjerrum critical distance as the ion size parameter in the full Pitts equation. The results for pure water were obtained from the data of Stokes.[69,70] It was found that, for pure NM_2Py, the expanded equations were unable to provide a satisfactory fit of the data, consistent with the general breakdown of these equations with high values of κa; for NM_2Py, at a concentration of 0.01 M, $\kappa a = 0.45$.

For those solvents rich in water (25, 33, and 50 M%), it was noted that, as the HCl concentration was increased, the equivalent conductances also increased initially, then leveled out and decreased in the normal manner. This anomalous behavior is caused by a reduction in the ionic content of the solutions, and in the past, has been ascribed to adsorption of the electrolyte on the cell walls.[57] This, however, is a time-dependent process, and means that the measured resistance should increase with time. This was not noted to be the case, since once initial equilibrium had been reached after an addition, no drift in measured resistance was noted over a span of 72 hours.

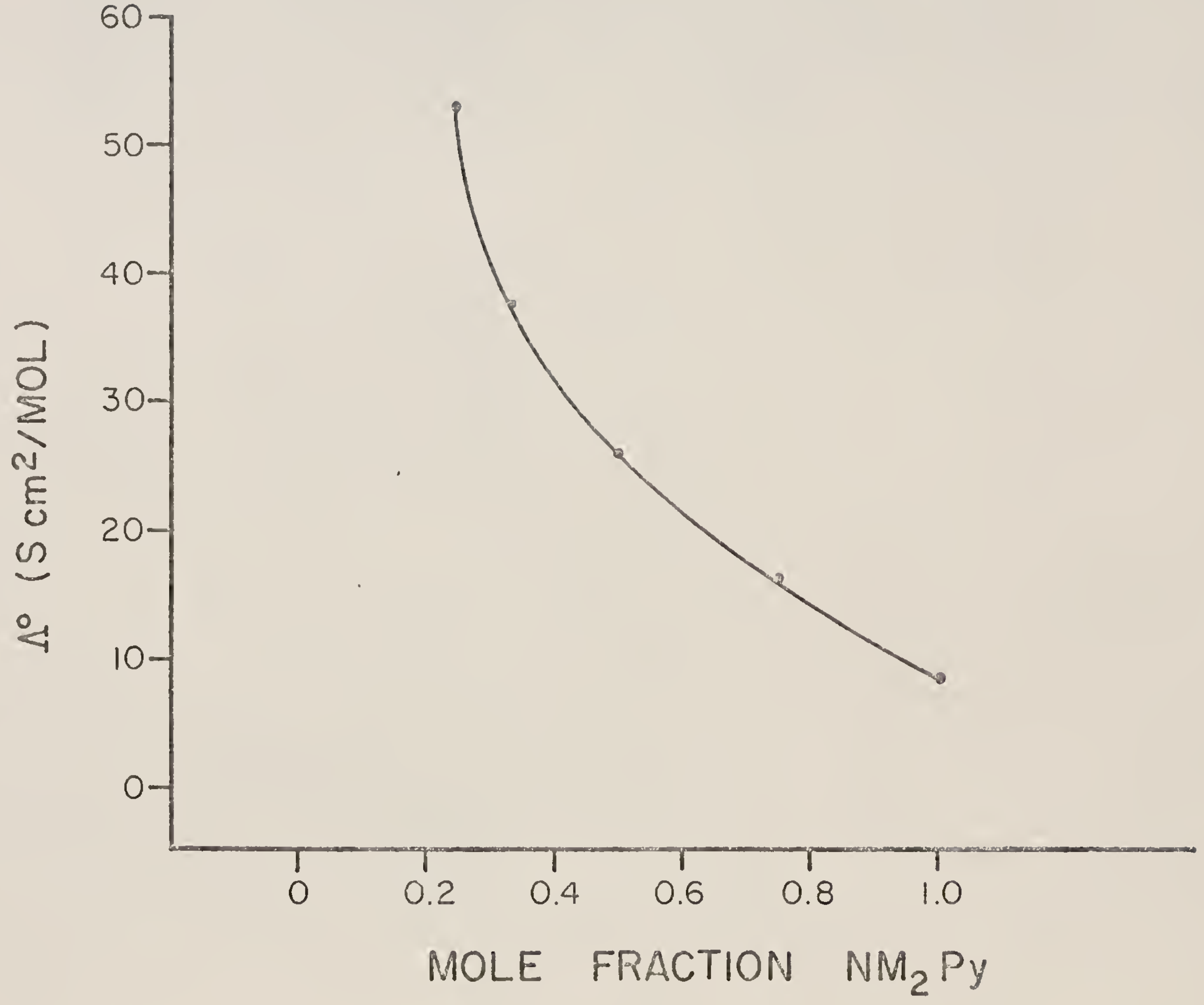
The reason for this strange behavior remains unknown. The conductance parameters were generated using those experimental points obtained after the maximum in conductance was reached. The initial loss of small amounts of electrolyte in the very dilute solutions should have little impact on the overall conductance results.

Figure 29 is a plot of the limiting equivalent conductance, Λ^o, vs. the mole fraction of NM_2Py in the solvent. It is evident that additions of small amounts of NM_2Py to water cause an extremely large drop in the limiting conductance of HCl, quite similar to the behavior observed for sulfolane; the decrease in conductance due to NM_2Py is greater still than that observed for sulfolane.

As was previously pointed out, the reason for such a large decrease in Λ^o with the addition of the nonaqueous component lies in the disruption of the water structure and the consequent elimination (for all practical purposes) of the proton jump mechanism. It has been shown[78] that NM_2Py is a structure breaker with respect to water, yet not as much of a structure breaker as sulfolane. Why then is the effect of adding NM_2Py to water greater than that of adding sulfolane?

Figure 29

A plot of the limiting equivalent conductance of HCl vs. the mole fraction of NM_2Py in the solvent at 25°C. The limiting equivalent conductance in water (0 mole fraction NM_2Py) is off-scale.


60
50
40
30
20
10
0
$\Lambda°$ (S cm^2/MOL)
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NM_2Py

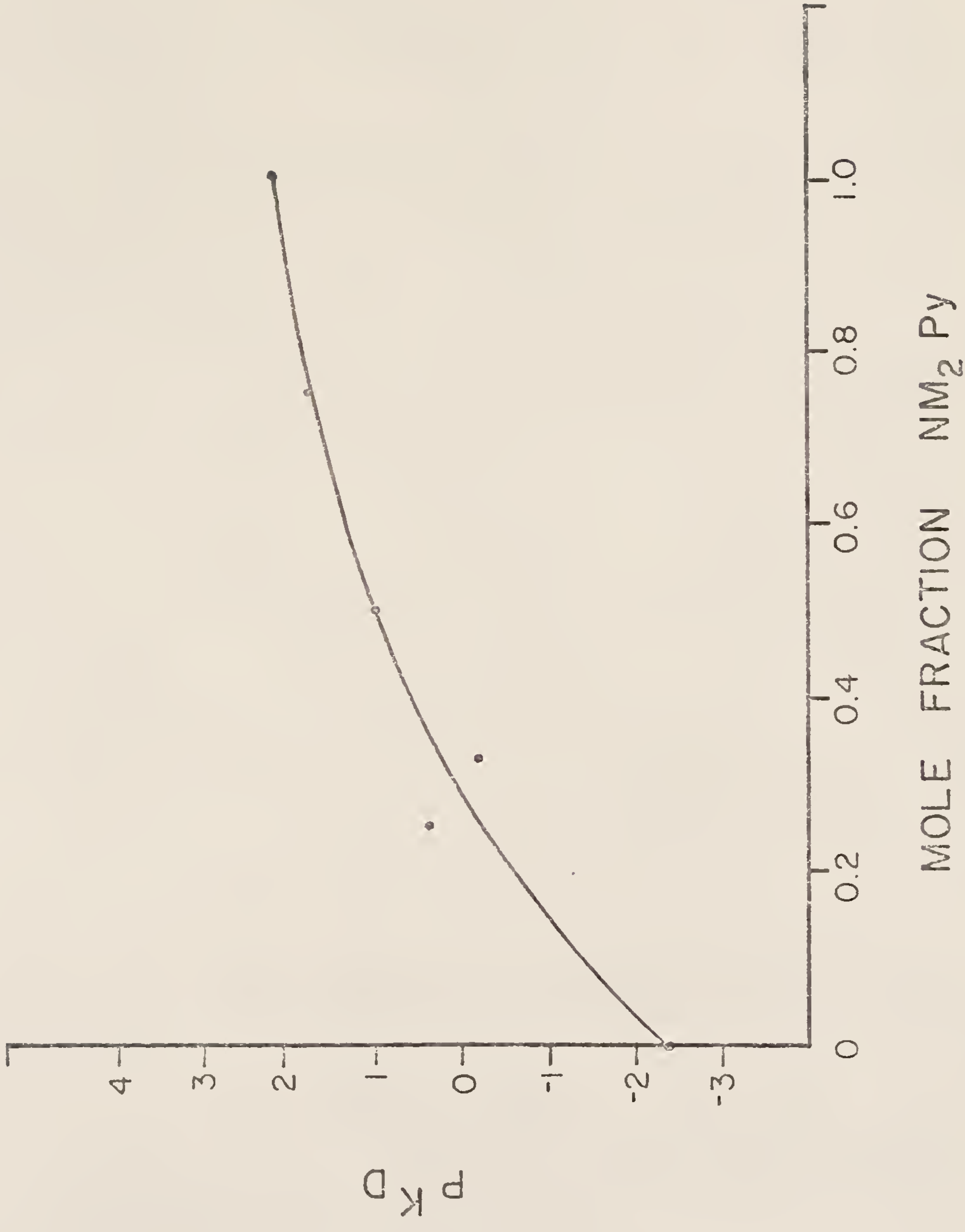
As shown in a previous section, NM_2Py associates strongly with water. Whereas adding sulfolane to water is a structure breaking process, evidenced by the negative curve for the excess viscosity, addition of NM_2Py to water is a structure making process. This can be seen in the large positive excess viscosity. While the water structure is being disrupted, the over-all structuring in the solvent is on the increase. This structure, however, evidently does not lend itself to a proton jump mechanism, and thus the limiting conductance decreases. In addition, the large increase in viscosity, in and of itself, helps decrease the limiting conductance by decreasing the ionic mobility. These two facts together indicate that the structure within the solvent is probably the $NM_2Py \cdot 2H_2O$ entity, with little association between the individual entities.[13] Were aggregates of these entities to form, the probability of proton jump would be increased, and this is not noted.

Figure 30 is a plot of the pK_d (= log K_a) of HCl vs. the mole fraction of NM_2Py in the solvent. The outstanding feature of this plot is, first, its over-all linearity, and second, the lack of any sharp increase at pure NM_2Py, as was noted for sulfolane. This is indicative of the essential difference between the two solvents.

As noted previously, sulfolane, with a pK_{SH^+} of -12.9, is highly protophobic, lending minimal solvation stability to the proton. NM_2Py, however, is quite different in this respect. Previous studies have shown that NM_2Py is far more

Figure 30

A plot of the pK_d (= log K_a) of HCl vs. the mole fraction of NM_2Py in the solvent at 25°C.


p K D
4
3
2
1
0
-1
-2
-3
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NM$_2$ Py

basic, with respect to the proton, than sulfolane,[127] which would indicate more of a tendency to solvate the proton. The measured pK_{SH^+} for NM_2Py is -0.17, indicative of the fact that, unlike the protophobic sulfolane, NM_2Py can and does protonate readily. This ability of the solvent to protonate (and thus stabilize the proton) is the principal reason that, in NM_2Py, HCl is a moderately strong acid, with K_a = 161.46 mol^{-1} L. The very low limiting conductance of HCl in pure NM_2Py is probably due to the lack of a proton jump mechanism coupled with the high viscosity, even more so than for the NM_2Py-water mixtures. As with sulfolane, anion solvation is expected to be small, although greater than in sulfolane due to a slight positive charge on the nitrogen.[128]

The linear dependence of pK_d on mole fraction NM_2Py in the middle region of Figure 30 can probably be attributed to the greater stabilization (by solvation) of the proton with increasing water content. This solvation would be primarily by the species $NM_2Py \cdot 2H_2O$, which, apparently, is well able to stabilize the proton; in the solvent containing 50 M% NM_2Py, the K_a is only 10.40 mol^{-1} L, and by some treatments,[87] this is considered almost completely dissociated. For solvents with less than this mole fraction of NM_2Py, HCl exists primarily as a strong electrolyte.

For HCl in pure NM_2Py, the value of pK_a was found to be 2.8 by several methods,[79] in good agreement with the value of 2.2 obtained in this study. By contrast, the results of

Emelin and his coworkers,[126] yielding a value for pK_a of 4.08, are subject to question. Although their values for the equivalent conductances of HCl in NM_2Py are reasonable in light of the values obtained in this study, it is difficult to see how they arrived at a value for Λ^o of 33 S cm^2 mol^{-1}. The value obtained in this study, utilizing the full Pitts equation, was 8.848 S cm^2 mol^{-1}, quite reasonable in view of the constituent equivalent conductances. A value of 33 suggests a conductimetric behavior of Type V, and this is clearly not the case.

Once again, the electrostatic theories of association show their weakness. For those systems where HCl is a moderately strong electrolyte, the Bjerrum theory of association can provide a fair prediction of the association constant. Where HCl is a weak electrolyte, the theory breaks down. For 0-, 25-, 33-, and 50-M% NM_2Py-water solvents, the Bjerrum K_a's are, respectively, 1.28, 3.31, 4.31, and 6.73 mol^{-1} L. At 75 M%, the predicted K_a of 12 mol^{-1} L compares poorly with the experimental value of 60.63 mol^{-1} L.

It is quite interesting to note that the method of variation of the ion size parameter, mentioned previously, was found to work, albeit poorly, for those systems where the Bjerrum theory provided a fair approximation of the experimental K_a. This was also found for the other solvent systems studied, as already mentioned.

There would thus appear to be a positive correlation between the ability of the Bjerrum theory to predict the association constant and a minimum in σ_Λ with variation of a. The Bjerrum theory best predicts the behavior of moderately strong electrolytes, and for these systems variation of a does produce a minimum in σ_Λ.[57] This may in part explain some of the confusion concerning the value chosen for a that has been seen in the past. For weak electrolytes, where the Bjerrum theory cannot predict the experimental K_a, the method of variation of a does not work, and thus, if the system under study includes a weak electrolyte, some other method for arriving at a value for a, such as the Bjerrum distance used in this study, should be used.

CHAPTER VII

CONCLUSIONS

Both sulfolane and NM_2Py are dipolar aprotic solvents with similar physical properties, yet they differ in one major aspect. Sulfolane, as reflected by its very low proton basicity, is protophobic, while NM_2Py can hardly be classified as such. This difference is manifested in the differing conductimetric behavior of HCl in the two solvents.

The limiting conductance of HCl was found to drop drastically with increasing sulfolane content in the solvent. This is attributed to the disruption, by sulfolane, of the water structure that supports the proton jump mechanism responsible for the high conductance of strong acids in water. The strength of HCl, as measured by the dissociation constant, was also found to decrease with increasing sulfolane content, but in a more moderate manner. The exception to this was in pure sulfolane, where the HCl was found to exist primarily in an associated form.

The full Pitts equation, using the Bjerrum critical distance as the ion size parameter, was able to provide a satisfactory fit of the conductance data for HCl in the sulfolane-water solvents at all temperatures studied. The exception to this was HCl in pure sulfolane, at 30 and 40°C.

These data were analyzed using the method of Caruso. At 30°C, homoconjugation was found, and prior work by Benoit has shown that the species formed is HCl_2^-. At 40°C, no evidence of homoconjugation was observed, and the conductance data were analyzed by using the extrapolation method of Shedlovsky and Kay. It is possible that this change in the dissociation process with temperature is caused by a decrease in the structuring of the sulfolane, which at 30°C retains much of the structure it had as a solid. The homoconjugation at 30°C is probably caused by the ability of sulfolane to solvate large ions coupled with very poor solvation of the anion, Cl^-. It is known that a number of homoconjugates such as $AgCl_2^-$ form in sulfolane.

Since almost all previous work with sulfolane has been done at 30°C, it is difficult to know what other effects (if any) are observed with rising temperature. The results of this study suggest that at 30°C sulfolane may not be a typical liquid dipolar aprotic solvent, and further work at elevated temperatures is needed.

The conductimetric behavior of HCl in NM_2Py-water solvents rich in water is very similar to the behavior noted in sulfolane-water mixtures. The limiting conductance of HCl fell rapidly with increasing NM_2Py content, attributable to the disruption of the water structure by NM_2Py. Both NM_2Py and sulfolane have been found to be water structure breakers, but it was noted that, whereas sulfolane caused a general decrease in solvent structuring, NM_2Py caused a marked increase in solvent structuring, attributable to the interaction between NM_2Py and water to form the associated species $NM_2Py \cdot 2H_2O$.

The ion association present in HCl solutions rose gradually with increasing NM_2Py content in the solvent, but even at 50 M% NM_2Py could be considered only slightly associated. HCl was found to exist as a moderately strong acid in pure NM_2Py. This may be attributed to the ability of NM_2Py to enter into hydrogen bonding at the carbonyl oxygen, and thus stabilize the proton by solvation. The low limiting conductance found for HCl in NM_2Py and NM_2Py-water solvents is believed to be caused by the lack of a proton jump mechanism, coupled with a high solution viscosity, and the possible formation of discrete hydrodynamic entities. As for sulfolane, and most other dipolar aprotic solvents, solvation of the anion is expected to be poor.

The 80 W% MetOH-H_2O solvent was found to foster slight association in the electrolytes studied, which are usually considered to be strong electrolytes. NaCl and HCl were found to be slightly associated, while NaAc and Tris·HCl were found to be associated to a slightly greater degree. HAc was found to be strongly associated, with a dissociation constant reasonable in view of that found in similar solvent mixtures using other alcohols. The larger pK_d found for the 80 W% MetOH-H_2O solvent may be caused by steric hindrance in the solvation of the proton, resulting from the larger size of the methoxyethanol molecule. The proton jump mechanism is noted, but in a very reduced form, and this has been explored by Thun.

Tris·HCl was also studied in water. It was found to be a strong electrolyte, essentially dissociated. The limiting conductance for the $TrisH^+$ ion was found to be smaller than expected. This is consistent with the ability of the $TrisH^+$ ion, with three OH groups, to hydrogen bond with the water structure. Transfer to the 80 W% MetOH-H_2O solvent caused an increase in ion association and a decrease in the limiting conductance. This is reasonable in view of the lesser ability of the mixed solvent to solvate the $TrisH^+$ ion.

It was noted that, for those systems where the electrostatic theory of ion association of Bjerrum was able to provide a fair approximation of the association constant, a minimum in the standard deviation of the conductance could be obtained by varying the ion size parameter. For those systems where the Bjerrum theory failed, so did the variation method. As a result, to be consistent, the Bjerrum critical distance was used throughout this study. Where the systems studied have moderate association approximated by the Bjerrum theory, the variation method of treatment appears to have merit.

APPENDICES

APPENDIX A---CONDUCTANCE DATA

APPENDIX B---COMPUTER PROGRAMS

APPENDIX A

CONDUCTANCE DATA

SOLVENT---25 M% Sulfolane-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
3.4981E-04	103.099
6.2844E-04	102.649
9.9713E-04	102.179
1.4132E-03	101.979
1.8148E-03	101.470
2.2121E-03	101.180
2.6116E-03	100.900
3.3772E-03	100.420
3.7757E-03	100.210
4.1563E-03	99.921
4.5339E-03	99.771

SOLVENT---25 M% Sulfolane-Water
TEMPERATURE--- 30 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
1.3886E-03	112.469
2.4728E-03	111.707
3.7505E-03	110.919
4.8106E-03	110.347
6.2202E-03	109.577
7.7413E-03	108.859
8.8779E-03	108.382
1.0112E-02	107.881
1.1308E-02	107.454
1.2536E-02	106.980
1.4135E-02	106.447
1.5442E-02	106.092

SOLVENT---25 M% Sulfolane-Water
TEMPERATURE--- 40 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
2.3435E-03	131.493
3.8634E-03	130.056
5.9749E-03	128.391
7.3956E-03	127.477
9.4757E-03	126.132
1.1179E-02	125.114
1.2948E-02	123.990
1.4602E-02	123.130
1.6615E-02	122.140
1.9484E-02	121.128
2.2091E-02	120.000
2.5953E-02	118.656

SOLVENT---50 M% Sulfolane-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
2.4543E-03	33.647
2.7605E-03	33.489
3.1395E-03	33.234
3.5024E-03	33.037
4.2715E-03	32.608
5.1971E-03	32.153
5.7115E-03	31.899
6.6713E-03	31.446
7.1798E-03	31.255
7.7786E-03	30.969

SOLVENT---50 M% Sulfolane-Water
TEMPERATURE--- 30 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.7056E-03	39.130
3.1260E-03	37.994
4.6395E-03	36.750
6.3705E-03	35.624
7.8767E-03	34.770
9.3374E-03	33.994
1.0844E-02	33.385
1.2363E-02	32.747
1.4034E-02	32.136
1.5823E-02	31.507
1.7826E-02	30.889
2.0621E-02	30.130

SOLVENT---50 M% Sulfolane-Water
TEMPERATURE--- 40 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.8125E-03	46.188
2.0720E-03	45.894
2.5791E-03	45.296
3.1078E-03	44.809
3.5393E-03	44.376
4.0950E-03	43.849
4.5835E-03	43.423
5.0959E-03	43.022
5.5862E-03	42.772

SOLVENT---75 M% Sulfolane-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
1.3943E-03	14.060
2.6590E-03	12.644
4.1185E-03	11.314
5.8971E-03	10.172
7.8847E-03	9.284
1.0373E-02	8.461
1.2904E-02	7.810
1.5524E-02	7.305
1.8919E-02	6.768
2.1870E-02	6.436
2.4834E-02	6.361

SOLVENT---75 M% Sulfolane-Water
TEMPERATURE--- 30 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
1.0817E-03	15.607
1.8025E-03	14.830
2.5500E-03	13.694
3.4895E-03	12.676
4.6936E-03	11.747
5.9074E-03	10.980
7.2180E-03	10.301
8.8548E-03	9.669
1.0214E-02	9.194
1.1791E-02	8.758
1.3485E-02	8.343
1.5766E-02	7.872

SOLVENT---75 M% Sulfolane-Water
TEMPERATURE--- 40 °C
SOLUTE---HCl

$c(\text{mol L}^{-1})$	$\Lambda(\text{S cm}^2\text{ mol}^{-1})$
1.3318E-04	25.324
4.0819E-04	23.608
7.6171E-04	22.133
1.1057E-03	21.039
1.4410E-03	20.087
1.8107E-03	19.069
2.2073E-03	18.214
2.5469E-03	17.627
2.8866E-03	17.123
3.2311E-03	16.612
3.5768E-03	16.166
3.9077E-03	15.788
4.2309E-03	15.430
4.5565E-03	15.108
4.9024E-03	14.766

SOLVENT---85 M% Sulfolane-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

$c(\text{mol L}^{-1})$	$\Lambda(\text{S cm}^2\text{ mol}^{-1})$
2.1200E-03	6.822
4.6748E-03	5.173
9.7251E-03	3.981
1.1215E-02	3.723
1.2971E-02	3.506
1.4923E-02	3.318
1.7203E-02	3.165
1.8653E-02	3.059
2.0380E-02	2.955
2.2615E-02	2.838
2.7113E-02	2.655
3.3252E-02	2.461

SOLVENT---85 M% Sulfolane-Water
TEMPERATURE--- 30 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
2.3228E-03	7.633
3.9677E-03	6.503
6.6773E-03	5.133
8.9155E-03	4.575
1.1130E-02	4.218
1.5784E-02	3.663
1.8941E-02	3.541
2.3524E-02	3.176
2.4246E-02	3.111
2.8467E-02	3.096
3.4505E-02	2.790
5.2333E-02	2.448

SOLVENT---85 M% Sulfolane-Water
TEMPERATURE--- 40 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
2.3419E-03	8.741
3.3141E-03	7.572
4.5002E-03	6.761
5.4610E-03	6.269
6.5112E-03	5.872
7.6747E-03	5.439
8.5836E-03	5.197
9.7424E-03	4.939
1.1434E-02	4.676
1.2571E-02	4.515
1.4119E-02	4.340

SOLVENT---100 M% Sulfolane
TEMPERATURE--- 30 °C
SOLUTE---HCl

$c(\mathrm{mol\ L^{-1}})$	$\Lambda(\mathrm{S\ cm^2\ mol^{-1}})$
1.7803E-03	0.267
4.5526E-03	0.238
5.4460E-03	0.234
6.8664E-03	0.225
8.4110E-03	0.222
1.1232E-02	0.223
1.4040E-02	0.224
1.7210E-02	0.226
1.9644E-02	0.227
2.2716E-02	0.228

SOLVENT---100 M% Sulfolane
TEMPERATURE--- 40 °C
SOLUTE---HCl

$c(\mathrm{mol\ L^{-1}})$	$\Lambda(\mathrm{S\ cm^2\ mol^{-1}})$
5.4732E-04	0.812
1.0673E-03	0.511
1.6745E-03	0.384
2.2722E-03	0.308
3.2895E-03	0.239
4.5549E-03	0.196
5.6198E-03	0.182
6.6298E-03	0.163
7.7673E-03	0.153
9.6316E-03	0.136

SOLVENT---25 M% NM2Py-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
2.0428E-03	49.751
4.2705E-03	50.230
5.4351E-03	50.275
7.1128E-03	50.047
8.2325E-03	49.886
9.3255E-03	49.403
1.0622E-02	49.185
1.1926E-02	48.990
1.3467E-02	48.757
1.5137E-02	48.512
1.7001E-02	48.243
1.8770E-02	48.040

SOLVENT---33 M% NM2Py-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.8722E-03	32.784
3.3547E-03	34.744
4.8889E-03	35.259
6.4344E-03	35.320
8.0910E-03	35.312
9.9425E-03	35.106
1.1353E-02	35.004
1.2801E-02	34.884
1.4247E-02	34.773
1.5845E-02	34.647
1.7423E-02	34.513

SOLVENT---50 M% NM2Py-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
6.2246E-04	20.428
1.0941E-03	22.514
1.9876E-03	23.507
3.0661E-03	23.628
4.0665E-03	23.492
5.3296E-03	23.242
6.6524E-03	22.945
7.9587E-03	22.654
9.6281E-03	22.218
1.1138E-02	21.920
1.2467E-02	21.675
1.3784E-02	21.441

SOLVENT---75 M% NM2Py-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.0018E-03	14.397
1.8847E-03	13.346
2.9497E-03	12.762
3.9830E-03	12.342
4.8933E-03	11.934
5.8259E-03	11.627
6.6806E-03	11.287
7.6254E-03	10.998
8.5401E-03	10.744
9.5531E-03	10.448

SOLVENT---100 M% NM2Py
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.9017E-03	7.003
3.0819E-03	5.558
4.0778E-03	4.922
5.1046E-03	4.493
6.1461E-03	4.190
7.0249E-03	3.995
7.9772E-03	3.827
9.0077E-03	3.681
1.0449E-02	3.521
1.1856E-02	3.399
1.3189E-02	3.301
1.4758E-02	3.211

SOLVENT---80 W% MetOH-Water
TEMPERATURE--- 25 °C
SOLUTE---HCl

c(mol L^{-1})	Λ(S cm^{2} mol^{-1})
1.0308E-03	50.235
2.3159E-03	48.726
3.6672E-03	47.695
4.9493E-03	46.880
6.8956E-03	45.898
9.5516E-03	44.851
1.1168E-02	44.328
1.2813E-02	43.833
1.4667E-02	43.387
1.6899E-02	42.881
1.8978E-02	42.455
2.2214E-02	41.892

SOLVENT---80 W% MetOH-Water
TEMPERATURE--- 25 °C
SOLUTE---NaCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
8.8831E-04	29.752
1.6551E-03	29.035
2.3491E-03	28.542
3.1126E-03	28.098
3.8850E-03	27.727
4.7360E-03	27.357
5.7255E-03	26.999
6.6050E-03	26.707
7.5226E-03	26.433
8.6949E-03	26.117
9.9230E-03	25.823
1.1851E-02	25.418

SOLVENT---80 MetOH-Water
TEMPERATURE--- 25 °C
SOLUTE---NaAc

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
9.3058E-04	23.958
1.2630E-03	23.676
1.6773E-03	23.362
2.0625E-03	23.101
2.6014E-03	22.773
3.7400E-03	22.183
4.6878E-03	21.768
5.6674E-03	21.397
6.6449E-03	21.069
7.3989E-03	20.839
8.4268E-03	20.554
9.8518E-03	20.194

SOLVENT---80 W% MetOH-Water
TEMPERATURE--- 25 °C
SOLUTE---TrisHCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
1.0193E-03	24.868
2.4322E-03	23.686
3.7122E-03	22.927
4.5503E-03	22.523
5.4897E-03	22.126
6.2258E-03	21.845
7.0050E-03	21.576
8.1082E-03	21.235
9.3267E-03	20.892
1.0713E-02	20.541
1.1796E-02	20.293
1.3009E-02	20.038

SOLVENT---80 W% MetOH-Water
TEMPERATURE--- 25 °C
SOLUTE---HAc

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
1.4286E-03	0.033
2.5720E-03	0.033
3.9471E-03	0.035
5.3867E-03	0.032
6.6175E-03	0.032
8.1364E-03	0.031
9.2652E-03	0.030
1.1008E-02	0.029
1.2341E-02	0.029
1.3441E-02	0.029

SOLVENT---Water
TEMPERATURE--- 25 °C
SOLUTE---Tris·HCl

c(mol L^{-1})	Λ(S cm^2 mol^{-1})
3.8086E-04	104.878
4.3331E-04	104.808
6.4097E-04	103.779
9.8939E-04	103.469
1.2467E-03	102.929
1.4537E-03	102.809
1.5429E-03	102.809
1.8155E-03	102.869
1.9323E-03	102.239
2.1055E-03	101.810
2.2491E-03	101.760
2.2803E-03	101.940
2.3112E-03	102.279
2.9637E-03	101.590
2.9674E-03	101.310
3.4152E-03	100.700
3.6500E-03	100.620
3.7873E-03	100.890
4.8032E-03	99.789
4.8078E-03	99.883
6.3979E-03	99.032
6.6171E-03	98.838
7.4038E-03	98.502
7.7206E-03	98.449
8.3647E-03	98.095
8.7773E-03	97.997
9.3236E-03	97.721
9.5604E-03	97.712
9.9768E-03	97.467
1.0202E-02	97.449
1.1058E-02	97.066
1.1061E-02	97.139
1.1907E-02	96.798
1.2002E-02	96.831
1.2711E-02	96.902
1.2879E-02	96.560
1.3707E-02	96.237
1.3735E-02	96.292
1.4884E-02	95.993
1.4908E-02	95.909
1.5952E-02	95.615
1.6109E-02	95.633

SOLVENT---Water
TEMPERATURE--- 37 °C
SOLUTE---Tris·HCl

$c(\mathrm{mol\ L^{-1}})$	$\Lambda(\mathrm{S\ cm^{2}\ mol^{-1}})$
7.1244E-04	131.035
1.0081E-03	130.355
2.1840E-03	128.506
2.6237E-03	127.947
3.7574E-03	126.977
4.6154E-03	126.257
5.0611E-03	125.968
6.1003E-03	125.288
7.2061E-03	124.628
7.8365E-03	124.308
8.8483E-03	123.689
9.4913E-03	123.399
1.0604E-02	122.859
1.0870E-02	122.739
1.1411E-02	122.509
1.1810E-02	122.319
1.2318E-02	122.090
1.2846E-02	121.890
1.3355E-02	121.740
1.3761E-02	121.590
1.4954E-02	121.090
1.4990E-02	121.110
1.5620E-02	120.850
1.5660E-02	120.890

APPENDIX B

COMPUTER PROGRAMS

PITTSEQN/BAS

```
10 'PROGRAM BY S. DAVID KLEIN, DEPT. OF CHEM., UNIV. OF
 FLA., GAINESVILLE, FL  32611  USA
20 CLS
30 PRINT"            *** THIS IS THE PITTS EQUATION PROGR
AM ***"
40 PRINT:PRINT"THIS IS A REVISION. RESULTS OUTPUT TO PR
INTER ONLY!"
50 PRINT:PRINT"BE SURE TO ENTER ALL NUMBERS IN DOUBLE P
RECISION!"
60 PRINT:PRINT"COUNTER 'J' SETS # OF DATA SETS IN STATE
MENT 1090; COUNTER 'M'  SETS # OF ION SIZE ITERATIONS I
N STATEMENT 1080;  COUNTER 'K'   SETS# OF LAM-0 ITERATI
ONS IN STATEMENT 1060.":PRINT
70 DEFDBL A-H,O,Q-Z
80 DIM EC(25),EL(25),XL(25),QL(25),AL(25),CI(25),RC(25)
,YP(25),YQ(25),YR(25),EP(25),EQ(25),ER(25),TP(25),SP(25
),RL(25),D(25),Y(25),G(25),FA(25),QK(25),X(25),BL(25),C
L(25),DF(25),DS(25),TA(25),TB(25),TC(25),AK(25)
90 J=0
100 J=J+1
110 INPUT"INPUT DC,TEMP(K),VISC.,DENS.,MW SOLV.,MW.SOLU
.";DC,T,V,DE,MS#,MV#
120 PRINT"NOW INPUT THE # OF POINTS,THE APPROX. LAMBDA-
0"
130 INPUT N,OL
140 PRINT"INPUT THE CONCENTRATION,CONDUCTIVITY PAIRS."
150 FOR I=1 TO N
160 INPUT EC(I),EL(I)
170 EL(I)=0.999505D0*EL(I)
180 NEXT I
190 LPRINT"N=";N;"; DC=";DC;"; T(K)=";T;"; VIS=";V
200 LPRINT"DENS=";DE;"; MWSOLV=";MS#;"; MWSOLU=";MV#
210 LPRINT
220 FOR I=1 TO N:LPRINTUSING"EC=##.####[[[[   EL=####.#
###";EC(I),EL(I):NEXT:LPRINT
230 DB=DC*T
240 Z=DB:GOSUB 1600
250 A1=3.643252D6/(DB*Z3)
260 PRINT"ENTER A0 FOR THIS RUN."
270 INPUT A0
280 AP=1.158266D6/(DB*Z3)
290 BP=2.345787D13/(DB*DB*DB)
300 GP=82.34164D0/(V*(Z3))
310 HP=2.796299D6/(DB*Z3)
320 PRINT"INPUT THE A0 INCREMENT." : INPUT AI
330 M=0
340 Z9=Z3
350 M=M+1
360 A0=A0+AI
370 LPRINT"A0=";A0
```

```
380 BA=5.020330D9*A0/(Z9)
390 Z=2.0D0:GOSUB1600:RT=Z3
400 PRINT"AP=";AP,"BP=";BP,"GP=";GP,"HP=";HP,"RT=";RT,"
BA=";BA
410 PRINT:PRINT
420 K=0
430 K=K+1
440 FOR I=1 TO N
450 XL(I)=OL
460 QL(I)=XL(I)
470 AL(I)=EL(I)/QL(I) : CI(I)=AL(I)*EC(I) : Z=CI(I):GOS
UB 1600:RC(I)=Z3
480 YP(I)=BA*RC(I) : YQ(I)=1.707107D0*YP(I) : YR(I)=2.7
07107D0*YP(I)
490 Q=YP(I):GOSUB 1100
500 EP(I)=RE
510 Q=YQ(I) : GOSUB 1100
520 EQ(I)=RE
530 Q=YR(I) : GOSUB 1100
540 ER(I)=RE
550 Z=YP(I):GOSUB 1500:TA(I)=Z2
560 Z=YQ(I):GOSUB 1500:TB(I)=Z2
570 Z=YR(I):GOSUB 1500:TC(I)=Z2
580 TP(I)=0.75D0/(RT+YP(I))+(3.0D0/8.0D0)*(3.0D0*RT*TB(
I)*EQ(I)/(RT+YP(I))-2.0D0*TA(I)*EP(I))
590 ZK=((1.0D0+YP(I))*(RT+YP(I)))
600 SP(I)=(9D0*RT-10D0+YP(I)*(3D0*RT+1D0)+2D0*(YP(I)*YP
(I)))/(8D0*(ZK*ZK))-TA(I)*EP(I)/(4D0*(1D0+YP(I)))+(7D0*
RT*TC(I)*ER(I))/(16D0*((1D0+YP(I))*(1D0+YP(I)))*(RT+YP(
I)))+(RT*TB(I)*EQ(I))/(16D0*(1D0+YP(I))*(RT+YP(I)))
610 RL(I)=-OL*(AP*RC(I)/((1.0D0+YP(I))*(RT+YP(I)))+BP*C
I(I)*SP(I))-GP*RC(I)*(1.0D0/(1.0D0+YP(I))-AP*RC(I)/(((1
.0D0+YP(I))*(1.0D0+YP(I)))*(RT+YP(I)))-HP*RC(I)*TP(I)/(
1.0D0+YP(I)))
620 XL(I)=OL+RL(I)
630 D(I)=ABS(XL(I)-QL(I))
640 IF D(I) > 0.001 GOTO 460
650 Y(I)=EL(I)-RL(I)
660 ZT=((-A1*RC(I)/(1.0D0+BA*RC(I))))
670 Z=1.0D1:GOSUB 1390:ZM=ZT*Z2
680 Z=ZM:GOSUB 1500:G(I)=Z2
690 FA(I)=(DE/(DE+1.0D-3*EC(I)*((2.0D0*MS#)-MV#)))*(DE/
(DE+1.0D-3*EC(I)*((2.0D0*MS#)-MV#)))
700 G(I)=G(I)*FA(I)
710 QK(I)=(1.0D0-AL(I))/(((AL(I))*(AL(I)))*EC(I)*G(I))
720 X(I)=((EL(I)*EL(I))*EC(I)*G(I))/XL(I)
```

```
730 PRINT"I=";I:PRINT:PRINT"QL=";QL(I),"AL=";AL(I),"YP=
";YP(I),"YQ=";YQ(I),"YR=";YR(I),"EP=";EP(I),"EQ=";EQ(I)
,"ER=";ER(I),"TP=";TP(I),"SP=";SP(I),"RL=";RL(I),"XL=";
XL(I),"Y=";Y(I),"G=";G(I),"FA=";FA(I),"QK=";QK(I),"X=";
X(I):PRINT
740 NEXT I
750 SX=0 : SY=0 : ZX=0 : ZY=0 : ZZ=0
760 FOR L=1 TO N
770 SX=SX+X(L) : SY=SY+Y(L) : ZZ=ZZ+X(L)*Y(L) : ZX=ZX+(
X(L)*X(L)) : ZY=ZY+(Y(L)*Y(L))
780 NEXT L
790 PRINT"SX=";SX,"SY=";SY,"ZZ=";ZZ,"ZX=";ZX,"ZY=";ZY
800 AB=(N*ZX)-(SX*SX)
810 OL=((ZX*SY)-(SX*ZZ))/AB
820 SL=((N*ZZ)-(SX*SY))/AB
830 EZ=-SL
840 F=((ZZ-(SX*SY)/N)*(ZZ-(SX*SY)/N))/(ZX-((SX)*(SX))/N
)
850 Z=((ZY-(((SY)*(SY))/N)-F)/(N-2.0D0)):GOSUB 1600:SO=
Z3
860 Z=ZX/AB:GOSUB 1600:SB=SO*Z3
870 Z=N/AB:GOSUB 1600:SR=SO*Z3
880 SS=SR
890 FOR I=1 TO N
900 BL(I)=OL-OL*(AP*RC(I)/((1.0D0+YP(I))*(RT+YP(I)))+BP
*CI(I)*SP(I))-GP*RC(I)*(1.0D0/(1.0D0+YP(I))-AP*RC(I)/((
(1.0D0+YP(I))*(1.0D0+YP(I)))*(RT+YP(I)))-HP*RC(I)*TP(I)
/(1.0D0+YP(I)))
910 Z=1.0D0+4.0D0*EC(I)*G(I)*EZ:GOSUB 1600:AK(I)=Z3
920 AL(I)=ABS((AK(I)-1.0D0)/(2.0D0*EC(I)*G(I)*EZ))
930 CL(I)=AL(I)*BL(I)
940 DF(I)=EL(I)-CL(I)
950 DS(I)=DF(I)*DF(I)
960 NEXT I
970 SD=0
980 FOR L=1 TO N
990 SD=SD+DS(L)
1000 NEXT L
1010 Z=(SD/(N-1.0D0)):GOSUB 1600:SE=Z3
1020 LPRINT USING"LAM-0=###.###";OL;:LPRINTUSING"     S
D LAM-0=    ##.####[[[[";SB;:LPRINTUSING"     KA=##.###
#[[[[";EZ
1030 LPRINTUSING"SD KA=##.####[[[[";SS;:LPRINTUSING"
  SD LST SQ LINE=##.####[[[[";SO
1040 LPRINT
1050 IF K < 5 GOTO 430
1060 LPRINT "SD=";SE:LPRINT
1070 IF M <20 GOTO350
1080 IF J < 1 GOTO 100
1090 END
```

```
1100 REM * THIS IS FORT EXPI SUBROUTINE *
1110 IF (Q-1)<0 THEN GOTO 1200
1120 IFQ=0 THEN GOTO 1180
1130 R=1/Q
1140 AU=1.0D0-R*(((R+3.377358D0)*R+2.025216D0)*R+2.7094
79D-1)/((((R*1.072553D0+5.716943D0)*R+6.945239D0)*R+2.5
93888D0)*R+2.709496D-1)
1150 Z=-Q:GOSUB 1500
1160 RE=AU*R*Z2
1170 RETURN
1180 PRINT "SUBROUTINE BOMB...X=0"
1190 STOP
1200 IF (Q+3)<=0 THEN GOTO 1250
1210 AU=((((((((7.122452D-7*Q-1.766345D-6)*Q+2.928433D-5
)*Q-2.335379D-4)*Q+1.664156D-3)*Q-1.041576D-2)*Q+5.5556
82D-2)*Q-2.500000D-1)*Q+9.999999E-1
1220 Z=ABS(Q):GOSUB 1390
1230 RE=Q*AU-Z2-5.772157D-1
1240 RETURN
1250 IF (Q+9)<=0 THEN GOTO 1280
1260 AU=1-((((5.176245D-2*Q+3.061037D0)*Q+3.243665D1)*Q
+2.244234D2)*Q+2.486697D2)/((((Q+3.995161D0)*Q+3.893944
D1)*Q+2.263818D1)*Q+1.807837D2)
1270 GOTO 1310
1280 R=9/Q
1290 AU=1-R*(((R+7.659824D-1)*R-7.271015D-1)*R-1.080693
D0)/((((R*2.518750D0+1.22927D1)*R+5.921405D0)*R-8.66670
2D0)*R-9.724216D0)
1300 Z=-Q:GOSUB 1500
1310 RE=AU*Z2/Q
1320 RETURN
1330 END
1340 'DOUBLE PRECISION ROUTINES
1350 'COPYRIGHT TANDY CORP. 1978
1360 '
1370 '***NATURAL LOG***
1380 '
1390 Z2=LOG(Z):I0=0:I2=SGN(Z2):IF I2<0 Z=1/Z
1400 IF Z<1.065 THEN 1420
1410 GOSUB 1600:Z=Z3:I0=I0+1:GOTO 1400
1420 Z=(Z-1)/(Z+1):Z2=Z*Z:Z3=Z
1430 I3=9:GCSUB 1640:Z=Z+Z
1440 IF I0=0 THEN 1460
1450 FOR P=1 TO I0:Z=Z+Z:NEXT
1460 Z2=Z*I2:RETURN
1470 '
1480 '***EXPONENTIAL***
1490 '
1500 Z2=EXP(ABS(Z)):I0=0
1510 IF Z*Z<.004 THEN 1530
1520 Z=Z/2:I0=I0+1:GOTO 1510
1530 Z2=1:FOR I2=8 TO 1 STEP -1:Z2=Z2*Z/I2+1:NEXT
1540 IF I0=0 THEN 1560
```

```
1550 FOR P=1 TO I0:Z2=Z2*Z2:NEXT
1560 RETURN
1570 '
1580 '***SQUARE ROOT***
1590 '
1600 Z3=SQR(Z):Z3=(Z3+Z/Z3)/2:Z3=(Z3+Z/Z3)/2:RETURN
1610 '
1620 '***POWER EXPANSION SUBROUTINE***
1630 '
1640 Z2=Z*Z:FOR P=3 TO ABS(I3) STEP 2:Z3=SGN(I3)*Z3*Z2
1650 Z=Z+Z3/P:NEXT:RETURN
1660 END
```

EXPEQNS/BAS

```
10 'PROGRAM BY R. FERNANDEZ-PRINI & S. DAVID KLEIN, DEP
T. OF CHEM., UNIV. OF FLA., GAINESVILLE, FL  32601  USA
20 CLS
30 PRINT"THIS IS THE EXPANDED PITTS EQUATION PROGRAM."
40 PRINT:PRINT"RESULTS OUTPUT TO PRINTER."
50 DIM EC(25),EL(25),G(25),CL(25),CI(25),AS(25),DL(25),
DF(25),DS(25),AX(25)
60 INPUT"INPUT DC,T(DEG-K),V(POISE)";DC,T,V
70 INPUT"INPUT N,APPROX LAM-0,APPROX KA";N,OL,K1
80 PRINT"NOW INPUT THE CONC.-COND. PAIRS."
90 FOR I=1 TO N
100 INPUT EC(I),EL(I)
110 EL(I)=0.999505*EL(I)
120 NEXT I
130 LPRINT"EXPANDED EQUATION"
140 INPUT"INPUT A0 IN ANGSTROMS";A0
150 INPUT"INPUT A0 INCREMENT, # OF ITERATIONS";AI,Q
160 INPUT"FUOSS-HSIA OR PITTS(F OR P), WHICH TREATMENT"
;A$
170 LPRINT"N=";N;";  DC=";DC
180 LPRINT"T(K)=";T;";  V=";V : LPRINT
190 FOR I=1 TO N
200 LPRINTUSING"EC=##.####[[[[   EL=###.####";EC(I),EL(
I)
210 NEXT I
220 M=M+1
230 LPRINT:LPRINT"A0=";A0
240 IF A$="P" THEN LPRINT"PITTS TREATMENT":GOTO 260
250 IF A$="F" THEN LPRINT"FUOSS-HSIA TREATMENT" ELSE CL
S:PRINTCHR$(23)"WHICH TREATMENT DO YOU WANT, F(UOSS-HSI
A) OR P(ITTS)":FOR I=1 TO 1000:NEXT:CLS:GOTO 160
260 DT=DC*T
270 A=82.0460E4/(SQR(DT[3))
280 B=82.487/(V*SQR(DT))
```

```
290 A1=1.8246E6/(SQR(DT[3))
300 BB=5.029160E1*A0/SQR(DT)
310 S=A*OL+B
320 FOR I=1 TO N
330 AS(I)=EL(I)/(OL-S*SQR(EC(I)*EL(I)/OL))
340 NEXT I
350 E1=2.94257E12/(DT[3)
360 E2=4.33244E7/(V*(DT[2))
370 E=E1*OL-E2
380 BA=16.7099E4/DT
390 K=50.2916/SQR(DT)
400 BZ=BA/A0
410 IF A$="F" THEN GOTO 430
420 J1=2*E1*OL*(LOG(K*A0)+2/BZ+1.7718)+B*K*A0+2*E2*(0.0
1387-LOG(K*A0)) : GOTO 440 'THIS IS PITTS J1
430 J1=E1*OL*(1.8147+2*LOG(K*A0)+2*(2/BZ+2/(BZ[2)-1/(BZ
[3)))-E2*(1.5337+4/(3*BZ)+2*LOG(K*A0))+A*B+B*K*A0 : GOT
O 450 'THIS IS FUOSS-HSIA J1
440 J2=-(4*K*BA*E1*OL*(1.2929/(BZ[2)+1.5732/BZ)+B*((K*A
0)[2)+1.40725*(2*E2*K*A0)) : GOTO 460 'THIS IS PITTS J2
450 J2=-(E1*OL*K*A0*(0.6094+4.4748/BZ+3.8284/(BZ[2))-E2
*K*A0*(1.5405+2.2761/BZ)+E1*B*(2*(2/BZ+2/(BZ[2)-1/(BZ[3
))-1.9384)-B*E2*(4*1/(3*BZ)-2.2194)/OL+A*B*K*A0+B*(K*A0
)[2) 'THIS IS FUOSS-HSIA J2
460 S=A*OL+B
470 FOR I=1 TO N
480 CI(I)=AS(I)*EC(I)
490 AS(I)=EL(I)/(OL-S*SQR(CI(I))+E*CI(I)*LOG(CI(I))+J1*
CI(I)+J2*SQR(CI(I)[3))
500 CI(I)=AS(I)*EC(I)
510 G(I)=10[(-A1*SQR(CI(I))/(1+BB*SQR(CI(I))))
520 DL(I)=EL(I)-OL+S*SQR(CI(I))-E*CI(I)*LOG(CI(I))-J1*C
I(I)-J2*(SQR((CI(I))[3))+K1*G(I)[2*EL(I)*CI(I)
530 NEXT
540 S1=0:S2=0:S3=0:S4=0
550 FOR I=1 TO N
560 S1=S1-EL(I)*CI(I)*G(I)[2
570 S2=S2+EL(I)[2*CI(I)[2*G(I)[4
580 S3=S3+DL(I)
590 S4=S4-DL(I)*EL(I)*G(I)[2*CI(I)
600 NEXT
610 DZ=N*S2-S1[2
620 LI=(S3*S2-S1*S4)/DZ
630 KI=(N*S4-S1*S3)/DZ
640 OL=OL+LI
650 K1=K1+KI
660 PRINTUSING"OL=###.###   LI=###.###";OL,LI
670 PRINTUSING"KA=##.####[[[   KI=##.####[[[[";K1,KI
680 IF ABS(LI)>0.001 THEN GOTO 710
690 IF ABS(KI/K1)>0.001 THEN GOTO 710
700 GOTO 720
710 GOTO 370
720 FOR I=1 TO N
730 AX(I)=(-1+SQR(1+4*K1*G(I)*G(I)*EC(I)))/(2*K1*G(I)*G
(I)*EC(I)): IF ABS(AX(I)-AS(I))>0.0005 THEN AS(I)=AX(I)
:CI(I)=EC(I)*AS(I):G(I)=10[(-A1*SQR(CI(I))/(1+BB*SQR(CI
(I)))):GOTO730
740 CL(I)=AS(I)*(OL-S*SQR(CI(I))+E*CI(I)*LOG(CI(I))+J1*
CI(I)+J2*SQR((CI(I))[3))
```

```
730 AX(I)=(-1+SQR(1+4*K1*G(I)*G(I)*EC(I)))/(2*K1*G(I)*G
(I)*EC(I)): IF ABS(AX(I)-AS(I))>0.0005 THEN AS(I)=AX(I)
:CI(I)=EC(I)*AS(I):G(I)=10[(-A1*SQR(CI(I))/(1+BB*SQR(CI
(I)))):GOTO730
740 CL(I)=AS(I)*(OL-S*SQR(CI(I))+E*CI(I)*LOG(CI(I))+J1*
CI(I)+J2*SQR((CI(I))[3))
750 DF(I)=EL(I)-CL(I)
760 DS(I)=DF(I)[2
770 NEXT I
780 SD=0
790 FOR I=1 TO N
800 SD=SD+DS(I)
810 NEXT I
820 SE=SQR(SD/(N-2))
830 SL=SE*SQR(S2/DZ) : SK=SE*SQR(N/DZ)
840 LPRINTUSING"LAM-0=###.###  SD LAM-0=##.###";OL,SL
850 LPRINTUSING"KA=##.####[[[[ SD KA=##.###[[[[";K1,SK
860 LPRINTUSING"SD LAM=###.###";SE
870 IF M<Q THEN A0=A0+AI : GOTO 220
880 INPUT"DO YOU WISH TO CHANGE TREATMENTS(Y/N)";B$:IF
B$="Y" THEN GOTO 900
890 GOTO 920
900 IF A$="P"THEN A$="F":A0=A0-(Q-1)*AI:M=0:GOTO220
910 IF A$="F"THEN A$="P":A0=A0-(Q-1)*AI:M=0:GOTO220
920 END
```

SHEDKAY/BAS

```
10 'PROGRAM BY S. DAVID KLEIN, DEPT. OF CHEM., UNIV. OF
 FLA., GAINESVILLE, FL 32601 USA
20 CLS
30 PRINT"*** THIS IS THE SHEDLOVSKY-KAY EXTRAPOLATION P
ROGRAM ***":PRINT
40 DEFDBLA-O,R-Z
50 PRINT"ENTER ALL NUMBERS IN DOUBLE PRECISION!":PRINT
60 INPUT "INPUT CELL CONSTANT,SOLVENT RESIS";CC,SR
70 INPUT"INPUT DC,T,V";DC,T,V
80 Z=DC*T:GOSUB 990:DB=Z3
90 AL=8.203D5/((DC*T)*DB)
100 BE=82.43D0/(V*DB)
110 INPUT"INPUT N";N
120 FORQ=1TON
130 INPUT"INPUT C,RES";EC(Q),R(Q)
140 L(Q)=1000*CC/R(Q)
150 EL(Q)=1000*CC*((1/R(Q))-(1/SR))/EC(Q)
160 NEXT
170 L0=1000D0*CC/SR
180 A=3.649D6/((DC*T)*DB)
```

```
190 INPUT"INPUT LAMO";OL
200 Z=OL:GOSUB990:OP=Z3
210 FORQ=1TON
220 Z=EC(Q)*EL(Q):GOSUB 990:EK(Q)=Z3
230 Z(Q)=(AL*OL+BE)/(OL*OP)*EK(Q)
240 Z=1+(Z(Q)/2D0)*(Z(Q)/2D0):GOSUB990:SP(Q)=Z3
250 S(Q)=(Z(Q)/2D0+SP(Q))*(Z(Q)/2D0+SP(Q))
260 X(Q)=EL(Q)*S(Q)/OL
270 NEXT
280 FORQ=1TON
290 Z=10D0:GOSUB 820:LT=Z2
300 Z=EC(Q)*X(Q):GOSUB990:FM(Q)=Z3*(-A)
310 Z=FM(Q)*LT:GOSUB910:F(Q)=Z2
320 Z=F(Q):GOSUB990:F(Q)=Z3
330 K(Q)=EC(Q)*X(Q)*X(Q)*F(Q)*F(Q)/(1D0-X(Q))
340 Z=K(Q):GOSUB990:KN(Q)=Z3
350 Z=EC(Q):GOSUB990:SE(Q)=Z3
360 Z=(1-((L(Q)/EC(Q))*S(Q)/OL)):GOSUB990:OG(Q)=Z3
370 L(Q)=OL*KN(Q)*SE(Q)/(S(Q)*F(Q))*OG(Q)+L0
380 NEXT
390 FORQ=1TON
400 IA(Q)=SE(Q)/(S(Q)*F(Q))*OG(Q)
410 IB(Q)=L(Q)
420 NEXT
430 GOSUB 590
440 PRINT"SD OF 1ST APPROX LST SQ=";SD
450 L0=IN
460 FORQ=1TON
470 Z=(1-((L(Q)/EC(Q))*S(Q)/OL)*(1.0D0-L0/L(Q))):GOSUB9
90:LK(Q)=Z3
480 L(Q)=OL*KN(Q)*SE(Q)/(S(Q)*F(Q))*LK(Q)+L0
490 NEXT
500 FORQ=1TON
510 IA(Q)=SE(Q)/(S(Q)*F(Q))*LK(Q)
520 IB(Q)=L(Q)
530 NEXT
540 GOSUB 590
550 PRINT"SD OF 2ND LST SQR=";SD
560 K=(SL/OL)*(SL/OL)
570 PRINT"K=";K
580 END
590 'LEAST SQUARE SUBROUTINE
600 'X=IA   Y=IB
610 IE=0:IK=0:IG=0:IH=0:IJ=0
620 FORQ=1TON
630 IC(Q)=IA(Q)*IA(Q)
640 ID(Q)=IB(Q)*IB(Q)
650 IE=IE+IA(Q)
660 IK=IK+IB(Q)
670 IG=IG+IC(Q)
680 IH=IH+ID(Q)
690 II(Q)=IA(Q)*IB(Q)
700 IJ=IJ+II(Q)
710 NEXT
720 UZ=IE/N:VZ=IK/N
730 SX=(IG/N)-(UZ*UZ)
740 SY=(IH/N)-(VZ*VZ)
750 SL=((IJ/N)-(UZ*VZ))/SX
760 IN=VZ-(SL*UZ)
```

```
730 SX=(IG/N)-(UZ*UZ)
740 SY=(IH/N)-(VZ*VZ)
750 SL=((IJ/N)-(UZ*VZ))/SX
760 IN=VZ-(SL*UZ)
770 VA=((IH-(VZ*IK))-((SL*SL)*(IG-(UZ*IE))))/(N-2)
780 SD=VA/(IG-(UZ*IE))
790 RETURN
800 END
810 '*** NATURAL LOGARITHM ***
820 Z2=LOG(Z):I0=0:I2!=SGN(Z2):IF I2!<0 Z=1D0/Z
830 IF Z<1.065 THEN 850
840 GOSUB 990:Z=Z3:I0=I0+1D0:GOTO830
850 Z=(Z-1D0)/(Z+1D0):Z2=Z*Z:Z3=Z
860 I3=9:GOSUB 1010:Z=Z+Z
870 IF I0=0  THEN 890
880 FORP=1TOI0:Z=Z+Z:NEXT
890 Z2=Z*I2!:RETURN
900 '*** EXPONENTIAL ***
910 Z2=EXP(ABS(Z)):I0=0
920 IF Z*Z<.004 THEN 940
930 Z=Z/2D0:I0=I0+1D0:GOTO920
940 Z2=1:FORI2!=8TO1STEP-1:Z2=Z2*Z/I2!+1D0:NEXT
950 IF I0=0 THEN 970
960 FORP=1TOI0:Z2=Z2*Z2:NEXT
970 RETURN
980 '*** SQUARE ROOT ***
990 Z3=SQR(Z):Z3=(Z3+Z/Z3)/2D0:Z3=(Z3+Z/Z3)/2D0:RETURN
1000 '*** POWER EXPANSION SUBROUTINE ***
1010 Z2=Z*Z:FORP=3TOABS(I3)STEP2:Z3=SGN(I3)*Z3*Z2
1020 Z=Z+Z3/P:NEXT:RETURN
1030 END
```

FREQEXTR/BAS

```
10 DEFDBL A-H,J-Z
20 CLS
30 ' PROGRAM BY S. DAVID KLEIN, UNIV. OF FLA., DEPT. OF
 CHEM., GAINESVILLE, FL  32611 USA
40 ZZ=0
50 PRINT"THIS IS THE FREQUENCY EXTRAPOLATION AND EQUIV.
COND. PROGRAM"
60 PRINT"INPUT FREQUENCY,RESISTANCE PAIRS (FREQ. IN KHZ
)"
70 ZZ=ZZ+1
80 FOR I=1 TO 3
90 INPUT F(I),R(I)
100 FR(I)=F(I)*2*3.141592654*1000
110 F2(I)=FR(I)[2
120 NEXT I
130 Z=5.00003*(R(2)-R(1))/(R(3)-R(1))
```

FREQEXTR/BAS

```
10 DEFDBL A-H,J-Z
20 CLS
30 ' PROGRAM BY S. DAVID KLEIN, UNIV. OF FLA., DEPT. OF
 CHEM., GAINESVILLE, FL  32611 USA
40 ZZ=0
50 PRINT"THIS IS THE FREQUENCY EXTRAPOLATION AND EQUIV.
COND. PROGRAM"
60 PRINT"INPUT FREQUENCY,RESISTANCE PAIRS (FREQ. IN KHZ
)"
70 ZZ=ZZ+1
80 FOR I=1 TO 3
90 INPUT F(I),R(I)
100 FR(I)=F(I)*2*3.141592654*1000
110 F2(I)=FR(I)[2
120 NEXT I
130 Z=5.00003*(R(2)-R(1))/(R(3)-R(1))
140 A=(Z-1)/(F2(3)-(Z*F2(2)))
150 PRINT Z,A
160 FOR I=1 TO 3
170 B(I)=1/(1+(A*F2(I)))
180 NEXT I
190 M1=(R(1)-R(2))/(B(1)-B(2))
200 M2=(R(2)-R(3))/(B(2)-B(3))
210 M3=(M1+M2)/2
220 IF M3-M1>0.001 OR M3-M2>0.001 THEN 480
230 PRINT "STRAIGHT LINE OK"
240 IN#=R(2)-(M3*B(2))
250 PRINTUSING"INTERCEPT=######.## =R(S)";IN#
260 PRINT"NOW INPUT CONCENTRATION(MOL/GM SOL'N)TO GET M
OLARITY"
270 INPUT C
280 IF ZZ>1 THEN GOTO 310
290 PRINT"INPUT THE SOLUTION DENSITY SLOPE,THE SOLVENT
DENSITY."
300 INPUT SL,SD
310 MO=C*(SL*C+SD)*1000
320 PRINTUSING"MOLARITY= ##.####[[[[ MOLES PER LITRE.";
MO
330 IF ZZ>1 THEN GOTO 360
340 PRINT"INPUT THE SOLVENT RESISTANCE."
350 INPUT SR
360 RS=SR*IN#/(SR-IN#)
370 IF ZZ>1 THEN GOTO 410
380 PRINT"INPUT THE CELL CONSTANT."
390 INPUT CC
400 IF B$="Y" THEN GOTO 60
410 LA=1000*CC/(RS*MO)
420 PRINTUSING"EQUIV. COND.=####.#### S-CM[2/MOL";LA
```

```
430 PRINT
440 INPUT"CONTINUE WITH SAME RUN AND SAME CELL";A$
450 IF A$="N" THEN PRINT"SAME RUN, DIFFERENT CELL?" ELS
E GOTO60
460 INPUT B$:IF B$="Y" THEN GOTO 380
470 END
480 PRINT M1,M2,"pROBLEM HERE!"
490 END
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REFERENCES

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BIOGRAPHICAL SKETCH

Stuart David Klein was born in Brooklyn, New York, on November 22, 1954, the son of Sam and Evelyn Klein. He was educated in the New York City public school system, and was graduated with merit from the Stuyvesant High School in June of 1971. In September of that year he began undergraduate studies at the Polytechnic Institute of Brooklyn. During the course of those studies, he completed a thesis entitled: "Transfer Activity Coefficients of Tetraphenylgermane in Methanol-Water Solvents, n-Propanol, and Isopropanol" under the direction of Dr. David H. Berne. During his years at Poly, Mr. Klein was active in extracurricular affairs and was a member of the varsity fencing team.

Graduate work was begun in September of 1975 at Indiana University, under the direction of Dr. Dennis G. Peters. Ill health forced termination of those studies after nine months, and during the summer of 1976 Mr. Klein was employed by the Argus Chemical Company as a laboratory assistant.

In September of that year, graduate studies were started at the University of Florida, under the direction of Dr. Roger G. Bates. Those studies have continued until the present time.

Mr. Klein is a member of the American Chemical Society, the Analytical Division of the ACS, and is an associate member of the Society of Sigma Xi.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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